

INFLUENCES OF MINING ON WATER QUALITY

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Submitted to: **T. C. Brown**
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USDA Forest Service
Rocky Mountain Forest and Range Experiment Station
3825 E. Mulberry Street
Fort Collins, CO
80524

September 1999

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INTRODUCTION

Mining is essential to our society as it has developed. As high grade ores are depleted, exploration and development of lower grade ore reserves is inevitable. However, it is not inevitable that mining methods and procedures for pollution control remain as they have for the past 100 years. Environmental protection has become an important consideration in the feasibility, design, construction and operation of mining projects. Nature has not always deposited minerals at locations best suited to provide environmental protection, and precautions should be taken.

Mining activities, from extraction to processing, may disturb the environment. However, current legislative controls and guidelines have helped to minimize operational and post-operational effects from mining procedures. This has not always been the case as evidenced by the number of abandoned mine sites throughout the country. Although current legislation and restrictions on active mines reduce potential environmental disturbances, adverse impacts from abandoned mines can, in some instances, off-set advantages gained by active mine regulation.

Mining activities, especially abandoned sites, are recognized as potential sources of water quality contaminants. Mining has the potential to effect water quality chemically (metals, acidity, etc.) as well as physically (pH, suspended sediment, temperature, etc.). Water quality impacts from improperly operating systems or abandoned mine sites have been documented on-site. The off-site effects or consequences of these water quality impacts have not been investigated. Decisions about cleanup of past mining operations affecting water quality must rely on the assessment of the relation of mining to water quality, both on- and off-site.

There are many facets of the relation of mining to water quality that add complexity to this study. Some of these facets, which will be explicitly dealt with in this study, are (1) multiple

water quality parameters and the various associated water quality standards (2) various types of mining activities, (3) definition of dissolved versus total concentrations of water quality constituents, (4) the effects of water flow volume and timing on the concentration and transport of heavy metals, (5) the influence of surrounding geology and soils on the effects of mining on water quality, and (6) non-mining human sources of water quality degradation.

Study Objectives

1. Review the literature on the relation of mining and ore processing to downstream water quality.
2. Summarize the findings of case studies on the effects of mining activities on water quality.
3. Assess the feasibility of a large scale statistical analysis on the relation of mining on downstream water quality.

Objective 1. Review of literature on the relation of mining and related activities on downstream water quality.

INSTITUTIONAL STRUCTURE

The United States has a legacy of environmental damage caused by coal and hardrock mining. Much of this damage is manifested in water quality changes in surface and ground water resources. According to the U.S. Bureau of Mines, over 12,000 miles of streams have been contaminated by mining pollution, and the U.S. Environmental Protection Agency (EPA) claims 180,000 acres of lakes have been impacted from mining activities. According to EPA, hardrock mining alone has produced over 50 billion tons of waste in the United States, with 2 billion tons added each year (West et al., 1995).

The 1972 Federal Water Pollution Control Act (PL 92-500) contains several provisions that relate directly with mining operations. It established a national goal of eliminating the discharge of pollutants into the waters of the United States by 1985. Interim goals call for the application of best practicable control technology by 1977 and the best available technology by 1983. For a variety of reasons, none of these goals were achieved.

One of the more important provisions (Sec. 402) establishes a "National Pollutant Discharge Elimination System" (NPDES) through a waste discharge permit system. Every discharge to surface water requires a NPDES permit that sets forth effluent limitations and other control provisions.

The FWPCA (Sec. 303) also required the states to establish water quality standards for all surface waters. These standards describe water quality conditions that are acceptable to the states

and Federal government. The standards for turbidity, suspended solids and heavy metals have a direct effect on mining operations.

Federal Effluent Limitations

The Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) provides for the establishment of effluent limitations for specific types of industrial operations, including mining, and water quality standards for natural surface waters into which effluents are discharged. Applicable sections of the law are as follows:

1. Section 301 - places effluent limitations on industrial discharges in accordance with guidelines developed as required by Sections 304 and 306. The guidelines are applicable to specific industries, listed in Section 306, and must be specified in permits issued under the National Pollutant Discharge Elimination System (NPDES) of Section 402.

2. Section 302 - requires that effluent limitations (Section 301) be consistent with the attainment and maintenance of water quality (Section 303).

3. Section 303 - requires the setting of federally approved water quality standards, but encourages the setting of such standards by the states rather than the federal government.

Effluent limitations apply to the quality of the wastewater as it is discharged from a point source (ditch, outfall pipe, weir, spillway, etc.) To a surface water such as a stream or lake. The U.S. Environmental Protection Agency (USEPA) published interim effluent limitations and guidelines for the ore mining and dressing industry in November 1975 (USEPA, 1975b). These limitations apply to all types of mining except coal. The effluent limitations and guidelines also specify available control technology.

Limitations and parameters have been proposed for the various control technologies considered for specified ores as Best Practicable Control Technology Available (BPCTA) (Table 1). For example, all of the ores have a maximum limitation on total suspended solids (TSS) of 30 mg/L and a pH range requirement of 6.0 to 9.0 units. Specifically, however, the iron ore subcategory has an additional maximum limitation on iron (Fe) of 2.0 mg/L for both mines and mills, whereas the maximum limitation of Fe for a bauxite mine is 1.0 mg/L and additional maximum limitations on aluminum (Al) of 1.2 mg/L and zinc (Zn) of 0.2 mg/L exist. For iron ore mines, BPCTA is considered to be settling ponds with coagulation-flocculation and lime-neutralization as necessary to meet effluent limitations. For some types of iron ore mills, as opposed to mines, BPCTA is considered to be settling ponds with coagulation-flocculation systems while at others zero discharge is specified.

The general procedure followed by the EPA during the development of effluent limitations guidelines and standards of performance has been to visit a selection of operations for the industry involved so that representative conditions of wastewater characteristics and existing control technology may be determined.

As a general rule, the land owner assumes the responsibility of any problem resulting from the condition of the land at the time the owner takes title to the lands. In the case of unpatented mining claims on Federal land, the Federal agencies administering the land upon which the claim is located, are not legally responsible for the water pollution caused by an inactive mine on a claim. This is because a mining-claim perfected under the 1872 Mining Law, though unpatented, has the effect of a grant by the United States, and is regarded as property in the fullest sense of that term and may be sold, transferred, mortgaged and inherited without infringing any right or title of the

Table 1. Composite Summary of BPCTA* Interim Effluent Limitations and Control Technology.

<u>Parameter</u>	<u>Daily Maximum (mg/L)</u>	<u>Maximum Thirty Day Average (mg/L)</u>
Aluminum	1.2	0.6
Ammonia	60.0	30.0
Arsenic	1.0	0.5
Cadmium	0.1	0.05
Chemical Oxygen Demand	200.0 & 100.0 **	100.0 & 50.0 **
Copper	0.1	0.05
Cyanide	0.1 & 0.02 **	0.05 & 0.01 **
Iron	2.0, 1.0, & 0.2 **	1.0, 0.5, & 0.1 **
Lead	0.4	0.2
Mercury	0.002	0.001
Nickel	0.2	0.1
pH	Within range of 6.0 to 9.0 units	
Radium-226	10.0 pCu/L	3.0 pCu/L
Total Suspended Solids	30.0	20.0
Uranium	4.0	2.0
Zinc	1.0, 0.4, & 0.2 **	0.5, 0.2, & 0.1 **

*BPCTA: Lime precipitation and settling, pH adjustment, tailings impoundments, reuse of water, alkaline chlorination, zero discharge, filtration through sand and gravel tailings, secondary settling, ammonia stripping, wastewater - stream segregation, ion exchange, barium chloride coprecipitation, and coagulation-flocculation. (USEPA, 1975b).

**Value Dependent on Specific Ore, from USEPA, 1975b.

United States. The owner of the claim should therefore be responsible for pollution caused by inactive mines on the claim. However, if the owner of a mining claim should abandon their claim, the pollution problems on the claim would pass to the Federal government for possible abatement with little recourse, if any, against the claimant (USEPA, 1973).

There is no standard by which determination can be made as to what may be held to be an "action significantly affecting the quality of the human environment" (NEPA SS102(c)). Both state and federal governments have historically done a poor job preventing or stopping mining pollution. Where regulatory programs have been successful, public involvement has been key.

Mineral exploration, mine development, ore processing, and mine closure operations all have the potential to effect surface water quality. This report reviews these potential effects by mining commodity type.

MINING AND WATER QUALITY

Mineral Exploration and Development

Numerous environmental impacts have been attributed to the mineral extraction industry in general. These impacts, depending upon topography, geology, climatology, specific minerals involved, and mining techniques employed, may or may not have permanent adverse effects. Impacts resulting from haulage and access roads, drill holes, and air pollution are generally common, at least to a degree, in all mineral extractive industries.

After a mineral deposit has been located, specific information about the extent and grade of the deposit is required to evaluate the discovery and to assess mining feasibility. Potential water quality problems in this phase of mining are related to (1) access; (2) exploration involving drilling, trenching, and tunneling or sinking shafts; and (3) support facilities for both workers and equipment.

Heavy equipment and support facilities are required. The transportation of this equipment has the potential to affect water quality since access roads to an exploration site must be constructed with adequate consideration for environmental protection. Access across Federal land requires a special use permit for road construction from the appropriate land management agency. These permits usually specify how and where the roads are to be constructed. These same requirements do not apply to access roads constructed across private land or access roads on the mining claim being examined. Too often the "cheapest" type of access is utilized, and this access may also have the greatest environmental costs. Roads crossing streams with inadequate culverts may lead to road washouts; improper road location or cuts may initiate land slumping; and erosion that may be very difficult if not impossible to control. (USEPA, 1973). Toxic waste

materials used in road construction may result in near permanent pollution sources. Abandoned roads are easily eroded, causing siltation and sedimentation of receiving streams

It has been the general practice to dump excavated material from the construction of pits, trenches and cuts over the nearest hillside and to abandon the excavations after the desired information has been collected. These excavations can lead to accelerated erosion, the waste dumps may block or dam water courses, and the excavations can leave lasting scars on the topography. If these excavations are constructed on a mining claim of Federal land, they are a direct concern of the government as the mining company may abandon the claim and the scars, erosion and environmental damage then reverts to the Federal government and becomes a public liability (USEPA, 1973).

From a site closure or reclamation standpoint, it would be desirable to minimize the land surface disturbed by backhoes and bulldozers and to fill or restore all test excavations and revegetate the areas prior to site abandonment. If this practice is planned in advance, rock materials can be stockpiled during excavation and the task of restoration can be minimized.

Drill holes are often used in mineral exploration. These may range from small diameter diamond drill holes to large diameter test holes. If confined water is encountered, these wells may flow at the surface and discharge mineralized water to streams. The wells are often plugged with drilling mud or drill cuttings, but these materials do not normally form perfect seals. If the confined water breaks through to the ground surface after the site is abandoned it may become a source of water pollution. However, a mining company can adequately plug its test wells with cement grout.

In large bulk sampling tests, long tunnels, exploratory drifts, or deep shafts may be constructed. These openings are essentially mines, and pollution from mine drainage can occur. Mine drainage is a much more difficult problem to control than is filling a trench or sealing a drill hole. If a particular vein or joint is the source of mineralized water in the tunnel or shaft, it may be feasible to grout the joints or otherwise seal off the water-bearing zone to reduce the flow. This requirement would be similar to requiring an oil company to plug an oil test well to prevent salt water from polluting an overlying aquifer.

Mines are not greatly different from large wells in that they can drain or dewater the overlying or adjacent rock materials. The overlying or adjacent rocks may contain substantial quantities of pyrite (Fe S_2), a common sulfide mineral that is often associated with sulfide ore minerals. Water containing oxygen can percolate from the surface down through the dewatered rocks and react with the pyrite to form sulfuric acid. The acid water then seeps into the mine workings and discharges out the portal as acid mine drainage. The quality of water draining a mineralized area will generally be substantially more acidic after the construction of tunnels and drifts because of the resulting change in the ground water flow pattern (USEPA, 1973).

Many abandoned surface mine sites, and surface remnants of underground mining operations have been left with little or no reclamation and revegetation. As a result, vast unprotected surface areas remain exposed to the elements. These areas may range in size from an entire unreclaimed surface mine site to smaller wind erodible sites such as dried tailings ponds, spoil and mineral storage piles, and haul roads.

Water Resources Affected by Mine Operations

In underground mining there is always a certain amount of waste material that must be removed from the mine besides the waste rock. These wastes include seepage water which is often highly mineralized, industrial waste water used for dust control or drilling, drainage from sand filling operations, sanitary wastes, oil and grease, paper, wood and various containers.

Mines are designed and constructed so that liquid wastes and mine water will drain into some centrally located area where they are often allowed to settle in an excavated sump. The supernatant in the sump is pumped to the surface for disposal. In some deeper mines, drainage from the lower workings may be pumped to an intermediate level sump and pumping facility to overcome extremely high pumping pressures and to eliminate the necessity of pumping all of the mine drainage from the bottom of the mine.

Mine water often consists of both juvenile water and meteoric water. Juvenile water is new water that is produced or released by chemical reactions deep in the earth. This water is usually highly mineralized and in some cases may be similar to the solutions that deposited the ore minerals being mined. Meteoric water is derived from the atmosphere and can gain entry to the mine by percolating down through the overlying rock materials or through abandoned workings. Mine drainage of meteoric origin may have a marked variation in seasonal flow due to seasonal changes in precipitation and runoff. The rapidity of changes in the amount of mine drainage to changes in precipitation or runoff can be an indicator of the accessibility of surface water to a mine. The quicker the response, the greater the accessibility. In some cases, mine drainage can be reduced by management of the runoff in vicinity of the mine (USEPA, 1973).

Mine Drainage

Drainage from most inactive metal mines contains concentrations of dissolved metals. The most common metals of mine drainage are iron, manganese, zinc and copper. Most of the abandoned mines have relatively small flows and often have little or no effect on the receiving streams.

As a general rule, plugging or sealing a portal as a method of reducing or eliminating mine drainage will provide only temporary relief (USEPA, 1973). This kind of seal can result in even more serious pollution problems if the seal should fail or if the mine water should break out at some other location.

The best method of minimizing pollution from mine drainage is to prevent surface water from entering workings and sealing or grouting permeable zones encountered within the mine. These practices can also materially reduce the cost of pumping mine drainage from the mine. If these practices have not been attempted during mining operations, they should be done as a prerequisite to closing or abandoning the mine. Once a mine has been closed and flooded, it could be a very costly project to attempt to reduce the amount of drainage (USEPA, 1973).

In most cases it will not be feasible to attempt to reduce the flow of drainage from abandoned mines except where surface drainage has direct access to the workings. If it is desirable to correct a specific pollution problem, the treatment of the drainage may be the only practical solution. Treatment of drainage can usually be accomplished by diversion into a settling pond and, in some cases, pH adjustment.

Mine Discharge

Mine discharge is commonly characterized by high acidity, and high metal and sulfate concentrations, resulting from the oxidation of sulfate minerals to form sulfuric acid and mobilize metal ions. Major reduction in the pollution caused by mine discharge can be achieved by procedures such as reducing the flow of the water to the mines, reducing the exposure of sulfide minerals to the atmosphere, or by flooding abandoned mine workings to reduce the rate of sulfide oxidation. Common treatment techniques are neutralization and sedimentation, with further metal removal by precipitation of the remaining metals as metal sulfide. The precipitate may be smelted to recover various metals.

Milling Discharge

Waste from milling consists of a water stream, frequently containing dissolved toxicants, acting as a carrier for ground mineral fragments. These latter usually include metal sulfides, subject to oxidation if exposed to atmospheric conditions. Other materials of concern include reagents, such as cyanide, added to the milling circuit. The mill waste generally is alkaline.

Common treatment techniques utilized by the milling industry consist of discharging the slurry into a tailings pond, with sufficient detention to reduce the suspended-sediment concentration. The clarified water is then either decanted to receiving streams or, in an increasing number of cases, recycled as mill process water. The latter procedure is preferred for environmental considerations. The treatment considered in the development of the attached limits, for discharge to streams, consists of primary sedimentation in a tailings pond, as is currently practiced throughout the milling industry. Following sedimentation, it is anticipated that

the waste will be neutralized and treated for metals removal, as in the case of mine discharge, by sulfide precipitation.

Cyanide is frequently used in milling, both to dissolve gold and to prevent flotation of pyrite. Several other, less toxic, reagents are known to function equally as well as cyanide as a pyrite suppressant, and are recommended. Cyanide often decomposes during detention in a tailings pond. If the tailings pond decant contains high concentrations of cyanide, it is anticipated that the cyanide concentration will be reduced by the use of the alkali chlorination procedure.

Erosion and Leaching

Erosion and leaching of tailings from abandoned or inactive mines can significantly affect water quality. Erosion comes from surface streams flowing across the tailings and from streams flowing along the margins of the tailings ponds and eroding their sides. Land slides and slumping of tailings into a stream can also result in the sudden loading of toxic materials into the receiving water.

Leaching comes from water infiltrating into and flowing through the tailings. The leachates, which may be highly mineralized, tend to seep out near the margin of the tailings and create either a pollution problem near the tailings, or else at a remote location down the valley.

Other pollution problems associated with abandoned tailings include wind erosion and exhuming buried toxic chemicals by erosion. Wind erosion, besides creating an air pollution problem, can blow tailings into a stream or to a location where they are readily washed into a stream.

Waste chemicals are often collected in drums, and buried with the tailings during mining operation. Subsequent erosion of the tailings can bring these wastes to the surface where they can be washed into a stream. How much material has been buried in abandoned tailings ponds is not known.

Tailings Ponds

Tailings ponds are designed to intercept or capture runoff waters or collect sediment from areas of potential erosion. Tailings ponds may be designed for specific precipitation and/or streamflow events.

The developers of new mining projects often state that there will be no water pollution because all of the mill waste water will be recycled with no waste discharge from the tailings pond. This facility can only exist under certain climatic and hydrologic conditions. In areas where the amount of annual evaporation exceeds the amount of annual precipitation, it may be possible to construct and operate a non-overflow tailings pond. In areas where annual precipitation exceeds annual evaporation, all tailings ponds will eventually have a discharge. The discharge may be seasonal and occur only in the rainy season. All tailings ponds are suspected to have seepage discharges (USEPA, 1973).

In areas where evaporation is relatively high and precipitation is low, a tailings pond having a large surface area could operate as a "non-overflow" pond. The recycling of waste water from the tailings pond back to the mill would substantially reduce the size of the required pond. At some mines where the flow of mine water is large, the construction and operation of a "non-overflow" pond for the mill waste would be feasible only if mine water is treated and discharged separately.

The effluent from a tailings pond can generally be treated by careful pH adjustment followed by settling to remove the troublesome pollutants prior to its discharge to a stream. If a tailings pond dike should leak or contaminated water should seep into the ground through the floor of the pond, it may be impossible to prevent pollution of ground water of adjacent streams unless the ponds are sealed and stabilized to prevent leakage. Ground water pollution can be very serious. It is difficult to remove and will exist for a very long period of time.

These tailings ponds will certainly prove effective in removing the suspended materials from the mine and mill wastes, but leakage from these ponds through the dikes or through the underlying alluvium will create new and uncontrolled sources of water pollution. It is likely that the amount of seepage from older tailings ponds actually increases as the decant pipe is raised and the hydraulic gradient from the tailings pond to an adjacent stream is steepened. The treatment of the overflow from existing tailings ponds may prove inadequate to abate water pollution problems and it may become necessary for mining companies to seal or undertake other remedial action to reduce water pollution caused by leakage.

Tailings pond dikes and dam construction should follow the same engineering requirements that are employed in the design and construction of earth dams for the storage of water. Sites should be evaluated from the standpoint of safety and the structure should be designed to reduce leakage to a minimum and to prevent structural failure. Cutoff walls may be required beneath dikes and dams, earth materials used in construction should be evaluated in a soils laboratory for their suitability for use in the dam, and the moisture and compaction of the fill materials should be controlled during construction to prevent subsequent failure of the structure. Pre- and post-construction monitoring of hydrologic conditions should be mandatory. Some

states have regulations relating to the construction of earth dams for water reservoirs but these regulations are not generally applied to waste disposal ponds.

Normally, the decant pipe is used as an overflow for the pond and is raised in increments as the tailings pond is filled with sediments. If the entire holding capacity of a tailings pond is utilized for holding effluent, a longer retention time in the pond will increase pond efficiency in removing suspended materials. Filling existing ponds to capacity without first evaluating their safety as hydraulic structures is not recommended. Tailings ponds should also be constructed with emergency spillways to prevent overtopping of the dike or dam in case the decant pipe is plugged or collapses, or a torrential storm discharges an overload of runoff to the pond.

When the pond is filled with sediment, the mining company should revegetate or stabilize the sediments. Mill wastes are generally toxic to plants and some soil conditioning is required. This may include mixing the tailings with soil, possibly soil that was stockpiled when the pond was constructed, with sewage plant sludge, or with sand or other suitable material. A good growth of vegetation will reduce both wind and water erosion. If it is not feasible to revegetate, a one to two foot layer of mine rock spread over the surface of the pond will reduce both wind and water erosion. This material can be stockpiled near the pond during mining for use as cover material when the pond is full.

WATER QUALITY EFFECTS AND PARAMETER JUSTIFICATION

Water pollution is the most significant and long term environmental impact caused by mining. Pollution is something that is harmful and unwanted at a certain time and place (Wildeman, 1981). Over the years, state and federal laws were developed to control various types of water quality impacts from active mining (West et al., 1995). Legislative measures addressed point source (end of pipe) discharge limitations (water quality standards/criteria) and general water resource protection (alluvial valley floors).

Water quality is determined in part by the natural weathering processes which accompany the movement of water above, on, and under the earth's surface. Mining can affect water quality by changing the rate of natural processes due to alteration of geologic formations during the extraction of minerals. Additional water quality impacts are possible as a result of processing of ores. Wastewaters from processing mills may contain the residue of reagents used during ore concentration as well as the tailings from the processing operation. These water quality impacts can be classified into three broad groupings: physical, chemical, and biological (Zemansky et al., 1976).

Physical Effects

Physical water quality parameters include temperature, pH, dissolved oxygen, specific conductance, turbidity and suspended and total dissolved solids. These physical parameters are relatively easy to measure and can be used as an initial screen to determine if mining activities are effecting water quality (Tables 2 and 3).

Table 2. A summary of potential impacts associated with different types of mining activities.

Type of Mining	Potential Impacts
Sand and gravel	The major concern with sand and gravel mining is the increase in turbidity, suspended sediment, and color. These mining operations are generally quite close to or directly in the stream channels, so the potential for contamination is relatively high.
Quarries	Quarry mining has similar impacts to sand and gravel mining. Increases in turbidity and suspended solids may occur downstream from the operation. If the quarry is located in a limestone-dominated area, pH may increase.
Base metals	Many different base metals can be released into a stream from mining operations, including Zn, Pb, Ni, Cu, Mn, Fe, Mb, and Al. Lower pH values may occur below mine sites along with higher turbidity values and increases in chloride, sulfate, and conductivity. The lower pH values cause the metals to become mobile.
Precious metals	Mining for precious metals will have many of the same impacts mentioned above for base metals with another potential impact from cyanide leaching. Some precious-metal recovery operations use cyanide.
Oil shale	Both oil shale and tar sands mining create water quality problems similar to those of oil and gas operations. Increased values of sulfate, chloride, TDS, conductivity, and metals may result from the mining activity. Oil and grease may also drain into streams. Increases in turbidity and suspended solids are possible due to erosion.
Uranium	Radioactive materials that may contaminate streams include uranium, thorium, and radium-226. Heavy metals may also be released, the most common ones being Zn, Al, Mg, Cu, and Fe. Additional problems may include higher concentrations of sulfate, nitrate, chloride, phosphate, and ammonia.

Table 3. Water quality parameters and justification for assessing potential effects from mining operations.

Parameter	Justification
pH	a characteristic of water needed to assess the solubility ranges of the chemical parameters.
Specific Conductance	an indicator of the general quality of water; an indicator of the total dissolved solids.
Temperature	a characteristic of water needed to assess solubility ranges of the chemical parameters.
Dissolved Oxygen	an essential element for aquatic life; increases in major ion concentrations that may occur as a result of mining may affect the natural chemical oxygen demand, potentially causing oxygen depletion in a stream.
Total Suspended Solids	an indicator of suspended sediment in a stream; suspended sediment could act as a transport mechanism for heavy metals.
Total Dissolved Solids	an indicator of the general quality of water; concentrations often correlated to specific conductance.
Oil and Grease	an indicator of oil and grease.
Lithologic Classification	an indicator of general rock texture and type.
Textural Analysis % sand, silt, and clay	an indicator of textural variability; needed to assess erosiveness and suitability of rock material to be used as a plant growth medium; an indicator of the infiltration and water retention properties of spoils material.

Table 3. Continued.

Parameter	Justification
<u>Major Ions</u>	
Ammonia (NH_3)	a major component of ammonium-nitrate explosives commonly used at surface mines.
Bicarbonate (HCO_3^-)	needed to evaluate ion balances, alkalinity.
Calcium (Ca^{+2})	concentrations may increase in waters near surface mines; needed to evaluate ion balances; needed to calculate SAR.
Carbonate (CO_3^{2-})	an indicator of proper monitor well completion and reliability of ground water quality data.
Chloride (Cl^-)	a major component of chemical dust suppressants commonly used.
Magnesium (Mg^{+2})	concentrations may increase in waters near surface mines; needed to evaluate ion balances; needed to calculate SAR.
Nitrate-Nitrite (NO_3^- - NO_2^-)	a major component of ammonium-nitrate explosives commonly used; an indicator of spoils material suitability as a plant growth medium; a common constituent of fertilizers spread on reclaimed areas.
Phosphate (PO_4^{3-} as P)	a common constituent of fertilizers spread on reclaimed areas.
Sodium (Na^+)	concentrations may increase in waters near surface mines; needed to evaluate ion balances; needed to calculate SAR.
Sulfate (SO_4^{2-})	the predominant anion in acid mine drainage; concentrations may increase in waters near surface mines; needed to evaluate ion balances.

Table 3. Continued.

Parameter	Justification
Sulfur (S)	an indicator of the acid-base forming potential of spoils or refuse rock: % pyritic sulfur is an indicator of acid-forming potential; % sulfate sulfur is an indicator of base-forming potential; % organic sulfur is an indicator of the potential for spontaneous combustion of a mine's refuse pile.
% pyritic sulfur	
% sulfate sulfur	
% organic sulfur	
total sulfur	
<u>Trace Elements</u>	
Aluminum (Al)	a major component of clays; may become attached to suspended colloids; aluminum bound to clay colloids may clog gills in fish, resulting in suffocation.
Arsenic (As)	concentrations may increase in waters near surface mines; likely to have a higher than average concentration in coal and associated shales; may be a pollutant associated with fly ash disposal in surface mines.
Boron (B)	an indicator of the usefulness of spoils and refuse rock as a plant growth medium; concentrations may increase in waters near surface mines.
Cadmium (Cd)	concentrations may increase in waters near surface mines; may be a pollutant associated with fly ash disposal in surface mines.
Copper (Cu)	concentrations may increase in waters near surface mines; may be a pollutant associated with fly ash disposal in surface mines; change in Cu:Mo ratio could cause molybdenosis in livestock.
Iron (Fe)	most common metal transported by water; concentrations may increase in waters near mining activities.
Lead (Pb)	increased concentration reported in mine drainages.

Table 3. Continued

Parameter	Justification
Manganese (Mn)	increased concentration reported in mine spoils; concentrations may increase in waters near surface mines.
Mercury (Hg)	increased concentration reported in mine spoils water; may be a pollutant associated with fly ash disposal in surface mines.
Molybdenum (Mo)	may be a pollutant associated with fly ash disposal at surface mines; change in Cu:Mo ratio could cause molybdenosis in livestock.
Selenium (Se)	may be a pollutant associated with fly ash disposal at surface mines; coal commonly has a higher than average selenium concentration; selenium concentrations in coals and associated black shales are usually much higher than average; at a pH of about 8, selenite may be oxidized to the soluble selenite ion; harmful to livestock of in excessive concentrations.
Zinc (Zn)	concentrations may increase in waters near surface mines; may be a pollutant associated with fly ash disposal at surface mines.

The natural occurrence of total suspended solids (TSS) and turbidity in surface water is a function of the various hydrological and geological factors. If there are distinct seasonal variations in streamflows then turbidity will respond similarly. Generally, low values are seen for both TSS and turbidity with low flows. High values accompany the major flows and erosion. Lower values for nonglacially fed streams (approaching winter levels) occur during the summer except after precipitation events. After precipitation, there are temporary peaks for flow, TSS, and turbidity.

Chemical Effects

Mining, milling, and ore processing activities all have the potential to effect water quality. Potential water quality effects may be associated with different mining activities (Table 2). These are potential effects and should not be considered certain.

Likewise, a set of water quality parameters has been identified that may be used to assess potential effects from mining (Table 3). Water quality parameters specific to specific resource extraction or mining activities are presented later.

Many metals are micronutrients. That is, they are required in small concentrations for proper nutrition and their absence is detrimental to metabolism of many organisms. At higher concentrations, they exert a toxic effect. The toxicity of a metal is dependent on a variety of factors including other water quality parameters (pH, temperature, hardness, DO, turbidity, the presence of other metals or toxicants) and the species and condition of the organism. Acute toxicity may result from exposure to relatively high concentrations of some metals while lower concentrations produce chronic toxicity of a more subtle nature.

The physical impact on water quality includes the introduction of those solids which are measurable as settleable matter, suspended solids (technically referred to as nonfilterable residue), and turbidity. Soil erosion contributes to such introduction in several ways related to mining activity. Surface mining operations alter the land's surface and may decrease slope stability so that erosion increases. Erosion can be minimized by using optimum mining techniques such as contour block-out mining on steep terrain, careful disposal of overburden, prompt reclamation (i.e., revegetation binds and stabilizes disturbed soils), and diversion and treatment of surface runoff and subsurface drainage waters. Erosion may also result when waste material from underground mines or processing mills are improperly stacked. Frequently, these waste materials are transported as slurries. Direct discharge of such slurries to surface waters generally results in the introduction of high concentrations of solids. Settling or tailings impoundments may reduce this impact; however, further chemical treatment or filtration may be necessary in some cases.

The pH of most productive fresh waters is in the range of 6.5 to 8.5 and is a function of carbon dioxide and mineral content (Committee on Water Quality Criteria, 1972). Changes in pH may change the effects of some toxicants. For example, an increase in pH would result in less dissociation of ammonia and a corresponding increase in toxicity. Most species of fish cannot survive if the pH is reduced below 4.0 or raised above 9.5. The buffering capacity or resistance to change in pH is a further factor of importance since low alkalinity or a major reduction in alkalinity would allow greater pH changes (Committee on Water Quality Criteria, 1972).

Biological Effects

Like all land use activities, mining has the potential to effect aquatic biological resources. The most common effect is from sediment. Heavy concentrations of sediment can kill fish directly

by damage to their gills. The lethal concentration is dependent on the characteristics of the sediment and the species and condition of the fish (Koski, 1972).

Increasing damage to gill structures with increasing size, hardness, and angularity of particles (Ellis, 1944) and thickening of gill epithelium followed by death in rainbow trout exposed to several hundred ppm of TSS for extended periods was observed (Herbert and Merkens, 1961). Sediment in suspension can be heavy enough to injury fish directly by damaging their gills. Lethal concentrations vary considerably depending on the fish's age, general health, and the type of sediment particles in suspension. The duration of exposure to suspended sediments will also determine the amount of injury to the fish (Barnhart, 1975).

There is some evidence that the nature of the solids is important when considering biological type effects and that synergistic effects increase fish mortality when other toxicants are present. Water turbidity can be harmful to fish...directly if the suspended particles harm or block the gills. Fish may easily tolerate high turbidity for long periods except when the turbidity is accompanied by acids, alkalies, or substances that injure the gills and prevent their functioning normally (Huet, 1965).

TSS and turbidity cause direct adverse effects on fishes. The effect would be a function of the species of fish, the character and concentration of the solids, the presence of other toxicants, other water quality parameters, natural conditions for the species of fish in question, acclimatization, health and life cycle stage of the fish, and time of exposure. Likely effects are similar to those produced by other toxicants ranging from immediate mortality at high, acute concentrations to more subtle, long-term effects at lower chronic concentrations including gill epithelium changes, susceptibility to such diseases as fin-rot, and delayed mortality. If no other

toxicants are present, many species of fish can withstand extremely high suspended solids concentrations for short periods of time and will pass through highly turbid water. However, fish also exhibit avoidance reactions to turbid waters and, as with other toxicants, the introduction of solids may alter species distribution by eliminating sensitive species (Zemansky et al., 1976).

The biological response to chemical inputs is complex. Chemical inputs to waters may have no effect, chronic toxicity or acute toxicity. Toxicity measurements are species and often water type specific and no general findings are offered.

SAND AND GRAVEL

Sand and gravel excavations generally occur adjacent to or directly in river channels and their floodplains. Consequently, high turbidity values and sediment loads may appear downstream from a sand or gravel mining area. Other water quality constituents such as metals, pH, and conductivity, dissolved solids, and chloride can be affected by sand and gravel operations, depending on the type of material being excavated.

Water Quality Impacts

One important problem associated with sand and gravel mining within the stream channel involves the channel hydraulics and sediment load of the stream. Mining will cause changes in slope and flow pattern in the stream as well as alter the armoring layer of the bed and banks. These changes can result in scouring and deposition of the channel and potential erosion problems as the river adjusts to a new course. In many cases, the affected river has completely bypassed a segment of its normal channel and created a new channel as a result of sand and gravel mining.

Sand and gravel mining has severely disturbed many riparian ecosystems. Sand and gravel mining usually involves removing vegetation and topsoil, excavating gravels down to bedrock (or other layer) from the active floodplain, old terraces, and/or the active stream channel, and processing the gravel. The gravel processing may be for gravel or gold. Gravel processing for gravel alone usually involves a series of particle size sorting operations, often with a washing. The washing is to remove sand, silt, and clay and organic material from the desired gravel sized product.

Mine tailings piles have replaced much of the native streambed material. Riparian vegetation is absent along most channel bank and floodplain reaches. Floodplain soils, necessary

for vegetative recovery, are relocated in separate distinct piles, or absent altogether (Karle and Densmore, 1994).

A properly functioning riparian ecosystem is necessary for several water quality functions. The riparian vegetation roughness (stem density and litter layer) reduces overland flow velocities (from upslope conditions) and allows sediments to settle out since the kinetic energy is reduced. The decreased flow velocities allow the waters to infiltrate (enter the soil) and percolate through the soil. Nutrient concentrations of overland flow waters are usually decreased because the infiltrated waters are available for plant uptake or utilization by soil microbes. Further the riparian vegetation provides physical support to the stream bank (root density) and improves channel stability. The riparian vegetation also provides stream shading, a source of woody debris to the stream channel and allochthonous and autochthonous organic matter.

Unstable and/or excessively confined streambeds, over-steep floodplains, and other channel modifications have disconnected stream hydrology (and hydraulics) from the adjacent floodplain. Restoration efforts have long focused on reestablishing this linkage to improve or restore streamside or riparian vegetation.

Riparian recovery through natural processes is significantly hindered in these situations. In channel reaches where the stream bed is incised and straightened, bed scouring continues to occur. During flood stages, erosion of these unvegetated and unstable banks results in excessive sediment loading of the stream. This increased sediment load is then deposited in the channel downstream creating additional problems.

Natural river channels (disturbed and undisturbed) are dynamic. Six independent variables are considered to control the dimensions of natural channels. They include discharge, bedload

discharge, bed material size, bank material characteristics, valley-slope, and bank vegetation (Hey, 1978). Too often, vegetation restoration or site reclamation is attempted without proper understanding of the relation between streamflow - channel dynamics and the riparian vegetation. Reclamation efforts must first decide when to rely on natural recovery and where and how to manage recovery by altering or avoiding controlling factors to modify the pattern or increase the rate of ecosystem development.

Monitoring Recommendations

To determine whether mining is adversely affecting water quality conditions, certain key parameters often will indicate a stream-water impact. For example, an increase in concentration of such dissolved ions as cadmium, chloride, sodium, and zinc is reflected in increased conductivity values. Combining conductivity data with pH and total suspended solids data will yield basic information concerning mining-related impacts on stream water quality. A general review of the literature suggests that certain simple-to-measure parameters are good indicators of impacts caused by most mining operations. These parameters are pH, conductivity, temperature, suspended solids, and discharge (Wildeman, 1981). If noticeable changes occur in any of the above parameters and mining operations are located upstream, then more extensive water quality tests will be needed to better determine the cause of the changes.

Table 4. Parameter selection and rationale for sand and gravel mining (adapted from Kunkle and Johnson, 1987).

Parameter	Rationale
benthic macroinvertebrates	a biological analysis that integrates changes in physical and chemical water quality conditions
color	a general indicator reflecting chemical changes caused by mining
conductivity	a simple estimator of TDS
dissolved oxygen (DO)	an indicator of depressed oxygen levels caused by organic sediment loading
hardness	influences the toxicity of heavy metals to aquatic organisms
pH	a valuable measure for interpreting solubility ranges of chemical parameters
settleable solids	a simple indicator of the presence of materials that would settle on the stream bottom and potentially damage fish spawning habitat
total dissolved solids (TDS)	an index of inorganic pollutants in streams, TDS increases with increased ion concentrations (e.g., dissolved toxic metals)
total suspended solids (TSS)	an indicator of stream sediment transport. which can carry sorbed toxic metals
turbidity	a simple estimator of TSS

Regional Perspective

Most, if not all, sand and gravel mining operations require a water source for washing fines from the sand and gravel. The resultant wash water is turbid and usually held on site. The wash water is used repeatedly to remove fines. Most operations use a settling pond to allow the washed material to settle out and the clear water used again. The settling pond is usually small in volume and moves as the gravel pit moves. The sediment settling essentially seals the pond bottom and little surface water may seep into groundwater or reach the stream channel.

Water quality effects from sand and gravel mining operations are few, especially when best management practices (BMPs) are used. Water quality standard violations may occur during large precipitation events when settling pond storage capacities are exceeded. No off-site water quality effects have been measured consistently. Natural variability in downstream water quality, including turbidity and sediment transport mask any water quality effects specific to most sand and gravel mining operations.

PLACER MINING

Placer mining is where gold is sought in alluvial deposits in and along stream channels. In commercial operations, heavy equipment such as bulldozers, scrapers, loaders, and draglines are employed near the stream channel to move gravel and alluvial materials to sluice boxes or other gravity separation devices where the gold is removed. Large washing operations may use thousands of gallons of water per minute (Johnson, 1974). Though uncommon today, hydraulic stripping (use of water under high pressure) was often used in the past to forcefully remove the overburden.

Water Quality Impacts

Removal of gravel from the stream channel, washing of the alluvial materials, and deposition of spoil materials in the past have created severe water quality and fisheries degradation (Schneider, 1986). Wastewater from commercial placer mines is characterized by high levels of turbidity, settleable solids, and total suspended solids (USEPA, 1985; Levell et al., 1987). In addition, heavy metals such as arsenic that are released via overburden removal, sediment loading, and ore oxidation and runoff are sometimes resuspended in the water column during the mining operation (Carter and Hunt, 1981). Fortunately, these metals are often bound to particulate matter and can be removed with the efficient removal of settleable solids and with substantial reduction of total suspended solids, if these processes are part of the pollution-control operations (LaPerriere et al., 1985). Temporary holding ponds are often constructed along the stream (an undesirable practice) rather than above the floodplain for settling the turbid wash water (Levell et al., 1987). However, throughout the mining process, original vegetative cover will likely be destroyed by stream diversion and other movement of earth, and organic materials

commonly are introduced into the stream. A major problem results from mine abandonment with no reclamation or stabilization work, leading to long-term sediment deposition. Other impact sources include roads, diversion channels, small airstrips, camp or cabin sites, dams for water storage, and the movement of heavy machinery. Temporary living areas can be sources of human contaminants, solid wastes, fuel, oil, or chemical leaks (Kunkle and Johnson, 1987).

Monitoring Recommendations

Potential water quality effects from placer mining most often relate to physical site disturbance (similar to sand and gravel mining) (Table 5) with the potential heavy metals associated with the gold deposits (Table 6). Water quality parameters need to be selected on a case-by-case basis and an appropriate water quality monitoring plan developed.

Regional Perspective

Few placer mining operations exist outside Alaska. Recreational placer mining is increasing and water quality concerns have been expressed, but little monitoring has occurred to date. Given the relatively limited water quality database on placer mining, and restricted geographic occurrence, a regional perspective was not developed.

Table 5. A summary of common sources and impacts to water quality from placer mining mining (from Kunkle and Johnson, 1987).

Source	Characteristics and Impacts
Hydraulic stripping	The removal of overburden by hydraulic pressure has been responsible for heavy loading of sediments into streams, severely degrading water quality and fisheries habitat.
Ore-bearing materials removal	Use of trucks and heavy equipment in and around the stream channels can damage vegetation and wetland habitat in the riparian zone, destabilize the stream bank, alter stream hydraulics and ground-water flow, damage fish spawning areas, and contribute to water quality degradation by increasing turbidity and sediment loading. Water temperatures may increase, and fluctuations in dissolved oxygen levels can result from organic materials loading.
Washing/sluicing operations	These activities greatly increase turbidity, settleable solids, and total suspended solids. Most state water quality regulations necessitate that most sluicing operations utilize settling ponds to control settleable solids and reduce turbidity.
Settling pond construction and spoils disposal	The creation of settling ponds to reduce water pollution and the disposal of mine spoils can alter both the riparian zone and stream channel, causing loss of critical habitat. Although the construction of settling ponds is not allowed within the stream channel, poorly constructed ponds, unstable spoil piles, and diversions can contribute to increased sediment loading in the receiving water.
Enhanced recovery	Enhanced recovery operations such as cyanide heap leaching are presently being considered. These operations have to be carefully monitored on a site-specific basis to assure that toxic chemicals or heavy metals do not pollute local surface or ground waters.
Abandonment	Leaching from old mine tailings may produce metals, acids, cyanide, or solids. Recreational use, habitat, and aesthetic values may be adversely affected with the loss of natural stream features.

Table 6. Parameter selection rationale for placer mining (Kunkle and Johnson, 1987).

Parameter	Rationale
arsenic	arsenic-bearing rocks are typically found with gold deposits; dredging oxidizes and mobilized arsenic
benthic macroinvertebrates	a biological analysis that integrates changes in physical and chemical water quality conditions
color	a general indicator reflecting chemical changes caused by mining
conductivity	a simple estimator of TDS
copper	dredging oxidizes and mobilizes copper
dissolved oxygen (DO)	an indicator of depressed oxygen levels caused by organic sediment loading
hardness	influences the toxicity of heavy metals to aquatic organisms
iron	dredging oxidizes and mobilizes iron
lead	dredging oxidizes and mobilizes lead
mercury	used in amalgamation of free gold; dredging oxidizes and mobilizes mercury
pH	a valuable measure for interpreting solubility ranges of chemical parameters
settleable solids	a simple indicator of the presence of materials that would settle on the stream bottom and potentially damage fish spawning habitat
sulfate	an indicator of mining impacts in areas high in pyrite
temperature	a requirement for pH and conductivity and a valuable measure for interpreting solubility ranges of chemical parameters
total dissolved solids (TDS)	an index of inorganic pollutants in streams, TDS increases with increased ion concentrations (e.g., dissolved toxic metals)

Table 6. Continued.

Parameter	Rationale
total suspended solids (TSS)	an indicator of stream sediment transport, which can carry sorbed toxic metals
turbidity	a simple estimator of TSS

COAL MINING

Coal mining operations in the eastern United States tend to be underground operations, while the western United States have surface or open-pit operations (Hirgch et al., 1979; Slatick, 1980; NRC, 1981). Eastern coal with a higher sulfur content than western coal coupled with greater annual precipitation has resulted in more reported water quality problems (Plass, 1975; Larson, 1976; Minear and Tschantz, 1976; Rose et al., 1979; Skogerboe et al., 1979; Renn et al., 1980; Wilber et al., 1980; Betson, 1982; Cannon, 1983; Bevans, 1984; Hindall, 1984; Bloyd et al., 1986; Dick et al., 1986; Larson and Powell, 1986; USEPA, 1987; Jones, 1988; Powell, 1988; among many others).

In general, underground coal operations tend to follow the coal seam. Nonetheless, waste materials are produced and these materials provide a potential source of sediment from erosion as well as generation of acid mine drainage, both of which may impact water quality. Surface or open pit mining operations tend to have less acid mine drainage problems. Large areas of exposed subsoil and overburden materials have the potential to erode and generate sediment that may carry associated metals or other contaminants.

Since 1974, with the passage of the Surface Mining Control and Reclamation Act by the U.S. Congress, coal mine operations are required to have all runoff from the mine permit area pass through a sediment detention structure. The sediment detention structure requires a National Point Discharge Elimination System Permit (NPDES) and requires quarterly monitoring.

Water Quality Impacts

Coal mining and its associated activities create numerous threats to water quality. Many pollutants emanating from strip mines are toxic to fish, wildlife, and riparian vegetation. Low pH

levels, high color values, high turbidity, and excessive siltation not only diminish aesthetic values but also may seriously harm biological communities.

Mine-contaminated water can be too salty or acidic for irrigation, livestock use, or domestic purposes. Sediment from erosion of the unvegetated spoil piles can contribute to local flooding, create turbidity-caused treatment problems for municipal waters, harm aquatic habitat, and fill in reservoirs.

Sediment and water quality data were collected from two adjacent watersheds in northern Wyoming to compare some hydrologic differences between an undisturbed basin and a surface mined, but unrehabilitated basin (Ringen et al., 1979). Sediment yield was a better indicator of the mine disturbance than water quality. Other studies have had similar results, where suspended sediment was the better measure of water quality differences in mined versus unmined basins (Minear and Tschantz, 1976; Sedam, 1991; among others). Water quality differences were possibly related to streamflow generation mechanisms. Another study showed no measurable effects between watersheds surface mined for coal and unmined watersheds (Olsen and Dettman, 1976).

Numerous analytical techniques were applied to determine water quality changes in the San Juan River basin upstream of Shiprock, New Mexico as affected by coal mining and power generation activities (Goetz et al., 1987). With the available data it was not possible to identify any effects of the surface coal mines on water quality that were separable from those of urbanization, agriculture, and other cultural and natural changes. To identify specific causes of change in water quality, additional data collection at strategic locations is needed.

Lowflow water quality data from 779 sites in the coal bearing area of Ohio were classified according to land use. Land use classifications were unmined, abandoned mines (surface or underground) and abandoned reclamation (surface or underground). Watersheds with mining (surface or underground) or with reclamation had higher levels of specific conductance and sulfate than unmined basins (Hren et al., 1984). Mining also affected pH, alkalinity, acidity, total and dissolved iron, and total manganese. Reclamation returned levels of these properties and constituents to near unmined conditions (Hren et al., 1984) and Childress, 1984). Portion or percentage of basin mined could be used to estimate sulfate concentrations in surface waters (Bevans, 1984).

Mine water quality data from abandoned and flooded coal mines in the Western Middle Coal Field in East-Central Pennsylvania suggested that water temperature could be used as a clue for depth of circulation in the mine, and specific conductance as an index of total mineralization (Reed, 1987). Similar correlations were determined in the coal mining region of southwestern Indiana: dissolved solids and specific conductance; sulfate and specific conductance; and the seasonal patterns of water quality (Martin and Crawford, 1991).

The effects of surface and coal mining on water quality in southwestern Washington were determined with an above-below sampling comparison. Coal mining increased sulfate concentrations in surface waters, but did not effect stream pH. Total dissolved solids were observed to increase below mining activities. Elevated concentrations of dissolved iron and manganese generally correlated inversely with low dissolved oxygen and low streamflow (summer) conditions for all sampling locations (Fuste and Meyer, 1987).

The production of sulfate (and other constituents) and its transport to local streams is a complex process that involves the kinetics of the chemical reactions and the hydrology and geology of the area (Plass et al., 1975). Chemical transport models were developed for sulfate, calcium, conductance, turbidity, discharge and alkalinity. Calcium and sulfate were not correlated during the premine condition, but correlated after mining. The water quality parameter-hydrology link deserved further exploration.

Flow duration curves for streams draining surface mined land had lower variability than those draining unmined land in Illinois (Brabets, 1984). Surface mining changes basin characteristics such that peak flows are decreased and lowflows increased and these changes relate to area mined. Further, harmonic analysis of stream temperature showed higher harmonic means and lower amplitudes in surface mined basins.

Monitoring Recommendations

A few parameters are especially indicative of coal mining: TSS, pH, sulfate, conductivity, TDS, iron, and manganese (Rikard et al., 1986), (Table 7 and Table 8).

Table 7. A summary of common sources and impacts to water quality associated with coal mining. (adapted from Kunkle and Johnson, 1987).

Pollution Source	Characteristics and Impacts
Mine shafts	Seeps from mine shafts may have an orange to yellow color, low pH (<3.0), high conductivity, and high concentrations of substances such as sulfate, iron, aluminum, manganese, and chloride.
Strip mines	Erosion from barren strip-mined areas will increase turbidity downstream following precipitation. Seepage from the spoil areas may have the same characteristics as mine shaft seepage.
Ponds	Runoff water from strip-mined areas that accumulates in ponds is typically coffee-colored and acidic, and it contains the high metal concentrations typical of acid mine drainage.
Roads	Both new and abandoned roads can erode, causing landslides and high turbidity and/or high sediment loads in streams.

Table 8. Parameter selection rationale for coal mining (Kunkle and Johnson, 1987).

Parameter	Rationale
acidity	a measure of the strength of acids and aluminum and iron sulfates released during mining
alkalinity	a measure of stream buffering capacity
aluminum	an indicator that depressed stream pH levels are mobilizing metals, a major component of clays
benthic macroinvertebrates	a biological test that integrates changes in physical and chemical water quality conditions
chloride	an indicator of mobilized alkaline earths and other chloride-bearing minerals
color	an indicator of dissolved metallic compounds (e.g., iron and manganese)
conductivity	a simple estimator of TDS
hardness	a factor in aquatic toxicity interpretation, reflects increased metal mobilization
iron	an indicator of iron oxide mobilization
manganese	an indicator of manganese oxide mobilization
mercury	an indicator of mercuric sulfate mobilization
pH	a valuable measure for interpreting solubility ranges of chemical parameters
potassium	an indicator of potassium-bearing rock mobilization
settleable solids	a simple indicator of the presence of materials that would settle on the stream bottom and potentially damage fish spawning beds
sulfate	a predominant anion that indicates the weathering of pyrite to sulfuric acid

Table 8. Continued

Parameter	Rationale
temperature	a requirement for pH and conductivity, and a valuable measure for interpreting solubility ranges of chemical parameters
total dissolved solids (TDS)	an index of inorganic pollutants in streams, TDS increases with increased ion concentrations (e.g., dissolved toxic metals)
total suspended solids (TSS)	an indicator of stream sediment transport, which can carry sorbed toxic metals
turbidity	a simple estimator of TSS
zinc	an indicator of zinc sulfide mobilization

Regional Perspective

Coal mining has the longest track record of all mining operations. So much coal mining has occurred and with water quality monitoring in these areas, that a large data base can be compiled. However, this data base does not clearly identify the effects of coal mining on water quality (Allison, 1988, among others).

The areal distribution of coal types in the conterminous United States have been delineated into six different 'coal provinces': Eastern, Gulf, Interior, Northern Great Plains, Pacific Coast, and Rocky Mountains (Powell, 1988). The weathering of iron pyrite which may be associated with the coal or associated strata may effect or degrade surface water resources. Surface and ground water resources in the Eastern and Interior Coal Provinces are generally not highly mineralized. This is a result of the precipitation exceeding potential evapotranspiration. Constituents are continually leached from the rocks and removed in low concentrations in streamwater. Dissolved constituents resulting from coal mine drainage are readily contrasted to background water quality (Powell, 1988). Water quality parameters included pH, total iron, total manganese, and dissolved sulfate. Other water quality parameters may indicate potential mine impacts, however these four parameters are routinely collected.

In the western United States (drier coal provinces) where potential evaporation exceeds precipitation, materials dissolved from minerals are moved toward the surface and concentrated in the upper soil or soil surface by evaporation. Flushing of these constituents by precipitation results in high concentrations of dissolved materials. In coal mine areas, the effects of coal mine effluent on streamwater quality are masked by the naturally occurring mineralized waters (Powell, 1988).

The constituent concentrations used as indicators of the influence of mine drainage on streamwater for the temperate East are not useful in evaluating similar effects in the West. Sulfate concentrations in surface waters are strongly influenced by acid mine drainage. However, the above referenced work evaluated upstream-downstream contrasts only. No off-site or large scale evaluations were done. Further, some of these watersheds may have relatively large atmospheric inputs of sulfate, since some coal mines were directly associated with an electric power generation station. Further, acid mine drainage abatement programs are now in place, whether active or passive treatment systems. Coal mining in the eastern United States is legally regulated to maintain water quality standards. Acid mine drainage may still be generated from abandoned systems. Land use activity maps are often inadequate to separate active mining operations from inactive or abandoned systems (Lee et al., 1987).

A regional analysis to separate or identify coal mining influences on water quality is doubtful. Water quality variability, common parameters influenced by other natural sources or land use activities and poorly identified hydrologic connections between the mine operation and streamflow generation mechanisms compound regional characterizations. The discriminant analyses methodology is data intensive, and probably not applicable to coal mining areas.

METALS

The most common impact of hard rock mining operations on water quality is probably acid mine drainage (AMD). Acid production may occur from mineralized rock, but for this study, acid generation was restricted to mine waters, especially since acid rock drainage (ARD) affecting water quality occurs less frequently than AMD.

Acid mine drainage (AMD) may be produced from sulfide mineral rock exposed as a result of mining, construction, or other activities to oxygen and water. The AMD waters are usually acidic, low to very low pH and have high metal concentrations. Metal solubility tends to increase with decreased solution pH values. AMD waters, as evidenced by iron and other metal precipitates were used as an exploratory tool for mineral exploration.

AMD from underground workings generally occurs as a point discharge, although regulated as nonpoint source. The discharge from drainage tunnels or mine adits may follow a complex route prior to reaching other surface waters.

Waste rock produced from mining operations is exposed to precipitation and runoff or other waters (seeps, etc.). Waste rocks containing sulfides (sulfide minerals) are potentially large sources of AMD. The chemical and physical properties of waste rock significantly affects the chemical quality of AMD and the source lifetime (time of AMD generation).

The Acid Generation Process

Acid mine drainage is produced by the exposure of sulfide minerals, commonly as pyrites, to oxygen and water, resulting in the production of acidity and increased concentrations of metals and sulfate. The sulfide is oxidized to sulfate and generates large quantities of acid in the process. Under most conditions, soil and geology overlying the sulfide deposit allow very little contact

with oxygen and water, therefore acid generation proceeds at a slow rate and the effect on water quality is negligible. When the rock is exposed to air and water by the mining process, the rate and quantity of acid generation is accelerated.

Total exclusion of moisture or oxidant will stop acid generation (Ladwig et al., 1984). In most cases, bacteria play a major role in accelerating the rate of acid generation, and the inhibition of bacterial activity in these cases will lessen the rate of acid generation.

The reactions of acid generation are best illustrated by examining the oxidation of pyrite (FeS_2), which is one of the most common sulfide minerals. The first important reaction is the oxidation of the sulfide mineral into dissolved iron, sulfate, and hydrogen (H^+):



The dissolved Fe^{2+} , SO_4^{2-} , and H^+ represent an increase in the total dissolved solids and acidity of the water, and, unless neutralized, the increasing acidity is often associated with a decrease in pH. If the surrounding environment is sufficiently oxidizing, much of the ferrous iron will oxidize to ferric iron:



At pH values above 2.3 to 3.5, the ferric iron will precipitate as $\text{Fe}(\text{OH})_3$, leaving little Fe^{3+} in solution while lowering pH at the same time.

The ability of a particular rock formation to generate acid is determined by the relative content of acid-generating and acid-containing minerals. The process by which acid is consumed is known as "neutralization." Acid waters produced by the sulfide oxidation in a rock may be neutralized upon contact with acid-consuming minerals. As a result, the water flowing from the rock may have a circa neutral pH and low metal concentrations. However, if the acid-consuming minerals are dissolved, washed out, or coated by other minerals, acid generation continues, and subsequent migration can occur. Whenever the acid-generation capability exceeds the acid-consuming capacity, it is generally expected that the drainage water will be acidic.

It is important to consider the temporal and spatial scale when investigating acid drainage. Rocks that produce near neutral pH conditions in drainage water, may experience acid generation in microenvironments around sulfide grains. The resulting acidic water may be neutralized by the remainder of the sample as it leaves the microenvironment. If an acid-generating rock has no neutralization potential, then acidic water will be present on the scale of both the sulfide grains as well as the rocks as a whole. A more complex situation occurs when pH-neutral water flowing over a rock invades and flushes the microenvironments of the sulfide grains, resulting in a slower rate of acid generation and a slower consumption of neutralization potential. To clarify terms, "acid generation" generally refers to the reaction in the microenvironment around a sulfide grain, whereas "acid mine drainage" refers to the chemical composition of water emanating from a rock or waste rock pile on a larger scale (Lewis, 1994).

The time interval between the initial disturbance of rock and the peak rate of acid generation may range from days to years, depending on a number of environmental factors and the neutralization potential of the rock. In addition, the rate at which acid generation occurs

through time will vary depending on several environmental factors and geochemical characteristics of the sulfide minerals. As a result, acid generation is not a simple process; rather, it is a complex set of chemical reactions changing through time (Lewis, 1994).

Water quality from any mining activity is the integration of geologic and hydrologic factors (Wildeman, 1981). These physical factors include ore petrology, ground water hydrology, and the physical occurrence of the ore in the ground. Ore quality is not a good predictor of water quality. The two major sources of constituents in mine effluent are the wall rock and the vein minerals. The base metals and sulfate are derived from the vein minerals and the abundance of pyrite in the veins. The wall rock and host rock determine the major metals.

Ground water systems may be classified as diffuse or conduit systems. The conduit system has water recharge localized in a few feeder pipes which may be faults or conduits formed by rock dissolution. Water chemistry in these systems respond to precipitation events and season changes (Wildeman, 1981). Diffuse system recharge is by seepage from small faults and voids. Water movement is slow and water chemistry usually shows little response to precipitation or seasons. Residence time is measured in months. If discharge does increase in the spring, constituent concentrations may increase rather than decrease (Wildeman, 1981); Stednick, unpublished). Water quality from a diffuse system may be predictable, more so than the conduit system.

Disseminated ore bodies often allow more intimate contact of the ground water with vein minerals and insures a diffuse flow aquifer. Veined ore bodies may have impervious rock to highly fractured rock which has a high porosity. The conduit system will have variable water

quality (Wildeman, 1981). Depth to water table may effect oxidation of the pyritic materials.

High water table maintenance may reduce oxidation and improve water quality.

Metal Leaching and Migration Processes

Low pH waters are capable of dissolving heavy metals (Felix et al., 1976, among others). In AMD, the metals are part of the mineral structure and the target of extraction processes. This water then migrates from the generation site and enters the receiving environment. A series of reactions occurs as the low pH water migrates from the source to the receiving environment. The resulting water quality is determined by several factors including: (1) nature of the sulfides and (2) availability and type of soluble constituents, (3) nature of alkaline reactants, and (4) physical properties of the waste.

Several naturally occurring physical, chemical, and biological properties of mine waste affect metal solubility and contaminant migration (Stumm and Morgan, 1990). The mobilization of metals is mainly controlled by chemical factors, while the processes that occur along the migration route are controlled by both physical and chemical factors.

Physical properties that influence metal solubility include waste particle size and shape, and temperature and pressure of pore gases. However, chemical factors are more predominant than physical properties in the metal mobilization process. Physical properties are important in the migration rate of AMD and in the reactions that occur along the migration path. Important characteristics include climatic conditions (temperature and precipitation), waste permeability/conductivity, pore water volume and pressure, streamflow/surface water generation and routing mechanisms.

These factors control the rate of metal movement, metal concentrations, and amount of dilution. The physical properties of the subsurface are different than those of waste, so a number of contaminant fronts (higher than ambient levels) may develop, all moving at different rates. Surface water contamination tends to occur before groundwater contamination because of lower retardation and the resulting rapid migration through the waste rock. The quality of the yields, whether surface or groundwater quality, is a function of the dilution and buffering reactions that occur en route.

The solubility of the metals is generally determined by the solution pH. Other chemical factors include the specific metal being dissolved, Eh, adsorption characteristics, and the chemical composition of the leachate. As the AMD moves away from the sulfide source through the waste material, more acid-generating material may be encountered, causing a reduction in pH.

The dissolved metal concentration generally increases as the solution pH decreases. However, a combination of chemical conditions may cause increasing mobilization of metals at neutral or even alkaline conditions. During the neutralization process of the drainage, precipitation of many of the soluble metals may occur, and the resultant drainage will contain the residual metals. A phenomenon observed in copper and massive sulfide ores is elevated zinc loadings in neutral drainage. Dissolved copper precipitates out as the pH is raised; the zinc remains at relatively high concentrations until the pH is raised to values above 9.5.

Biological activities along the route may also influence metal dissolution. Metal leaching occurs where iron-oxidizing bacteria are present with iron and metal sulfides. Biological species can also attenuate the mobility of metals by absorption and precipitation.

Cyanide Leaching

Some mining operations use cyanide leaching methods to recover gold and silver. Cyanide compounds of sodium and potassium are the most common leaching agents used in this form of mining. The cyanide solution is allowed to leach through the mined material and solubilize gold or silver, after which it drains into holding ponds or other structures. The precious metals are then recovered from the solution, while the waste cyanide solution may be recycled for later use.

Cyanide may seep into streams if holding structures are faulty or if eroded tailings containing cyanide are transported into the water (Stanton et al., 1986). While cyanide itself is highly toxic to humans and aquatic life, it breaks down rapidly at pH levels found in the natural environment. Therefore, toxicity to aquatic life might occur over a short distance downstream of a spill and would not be detected further downstream. A greater problem arises at cyanide leaching operations, where a spill could result in extensive heavy-metal contamination. Cyanide mobilizes a number of heavy metals associated with mine tailings, and the effect of such contamination would be felt much further downstream and for a longer period of time.

Monitoring Recommendations

Acid mine drainage (AMD) and acidic streams with high concentrations of metals are common. Many of these sulfide bodies are located in the uplifted mountains of the Western United States, where generally pristine waters may be impacted by the low pH and elevated metal concentrations. AMD lowers the solution pH and may increase concentrations of copper (Cu), iron (Fe), manganese (Mn), and molybdenum (Mo), lead (Pb) and zinc (Zn). Of these metals Cu is the most toxic to aquatic life (Forstner and Wittman, 1983).

Restoring systems impacted by AMD is difficult because of the often remote location of AMD impacted streams. Methods to control AMD involve either prevention of AMD at the source or treatment to remove acidity, metals, or sulfur. Prevention generally seeks to keep metal sulfide deposits from oxidizing or to keep water away from these materials. Treatment options include raising the solution pH, metal precipitation, or sulfur removal and include passive and active treatment systems.

Prevention generally involves keeping metal sulfides from coming into contact with the atmosphere and includes sealing mine adits, burying the sulfide material or capping these materials. Once the oxidation of sulfide materials begins, it is very difficult to arrest the process.

Treatment processes include raising the pH by CO₂ stripping or the addition of alkaline materials. Invariably metal precipitation flows, differences occur as to how the precipitate is treated: either disposed of as waste material or processed for the precious metal content.

In general, monitoring of pH and heavy metal concentrations can best determine the effects of metal mining on water quality. Other parameters are related to site disturbance effects (Table 9 and Table 10).

Table 9. A summary of common sources and impacts to water quality from hard rock mining.

Source	Characteristics and Impacts
Mine shafts	Mine drainage with sediment from mine working or acid mine drainage (AMD) low, pH, high conductivity, high metal concentrations.
Waste rock	Erosion potential and sediment delivery to nearby surface waters. Potential for AMD formation and movement.
Tailings	Erosion potential and sediment delivery to nearby surface waters. Greater potential for AMD formation and leaching.
Leach pads	Potential of leakage from heap leach pads includes AMD and cyanide or other leach formulation.
Roads	Roads can erode or landslide. Creating turbidity and high sediment loads.

Table 10. Parameter selection rationale for coal mining (Kunkle and Johnson, 1987).

Parameter	Rationale
acidity	a measure of the strength of acids and aluminum and iron sulfates released during mining
alkalinity	a measure of stream buffering capacity
aluminum	an indicator that depressed stream pH levels are mobilizing metals, a major component of clays
benthic macroinvertebrates	a biological test that integrates changes in physical and chemical water quality conditions
chloride	an indicator of mobilized alkaline earths and other chloride-bearing minerals
color	an indicator of dissolved metallic compounds (e.g., iron and manganese)
conductivity	a simple estimator of TDS
hardness	a factor in aquatic toxicity interpretation, reflects increased metal mobilization
iron	an indicator of iron oxide mobilization
manganese	an indicator of manganese oxide mobilization
mercury	an indicator of mercuric sulfate mobilization
pH	a valuable measure for interpreting solubility ranges of chemical parameters
potassium	an indicator of potassium-bearing rock mobilization
settleable solids	a simple indicator of the presence of materials that would settle on the stream bottom and potentially damage fish spawning beds
sulfate	a predominant anion that indicates the weathering of pyrite to sulfuric acid

Table 10. Continued.

Parameter	Rationale
temperature	a requirement for pH and conductivity, and a valuable measure for interpreting solubility ranges of chemical parameters
total dissolved solids (TDS)	an index of inorganic pollutants in streams, TDS increases with increased ion concentrations (e.g., dissolved toxic metals)
total suspended solids (TSS)	an indicator of stream sediment transport, which can carry sorbed toxic metals
turbidity	a simple estimator of TSS
zinc	an indicator of zinc sulfide mobilization

Regional Perspective

The environmental behavior of mineral deposits is defined as the suites, concentrations, residences, and availabilities of chemical elements in soils, sediments, airborne particulates, and waters that result from the natural weathering of mineral deposits and from mining, mineral processing, and smelting. Along with geochemical processes and biologically mediated processes, the geologic characteristics of mineral deposits exert fundamental controls on how the deposits and their mining or mineral processing byproducts interact with the environment. Other important controls, such as climate, topographic setting, and mining and mineral processing methods, generally modify the environmental effects mandated by mineral deposit geology and geochemical processes (Plumlee et al., 1994).

Most water quality effects or impacts tend to come from abandoned mine sites (Wildeman, 1976). The poorest water quality, most often low pH and high metal concentrations, is associated with disseminated ore systems (rather than veins) containing pyrite (Wildeman, 1976; Price et al., 1995).

Water chemistry at inactive and abandoned mines can be closely linked to ore deposit types (Plumlee et al., 1994; King, 1995). This can be illustrated by looking at metal concentrations as a function of pH, as pH decreases, metal concentrations tend to increase. Arsenic does not correlate with pH, because it is not transported in aqueous solution in the same types of complexes as most metals. However, arsenic can be correlated to the deposit type (Price et al., 1995). In general, water quality is predictable from geological knowledge about ore deposit type and mineralogy of ore and of associated wall rocks (Price et al., 1995).

Relating surface water quality to hard rock mining activities is more tenuous. Most water quality effects from hard rock mining are from inactive and abandoned mines, with acid mine drainage. Most mine drainages recharge over months and show little chemical response to precipitation or season (Wildeman, 1976). Nonetheless, AMD flow rates may or may not be constant, but flow volumes are low and are readily diluted by the receiving waters, especially if the receiving waters vary with precipitation events.

Metal concentrations will decrease with dilution by the receiving waters. However, probably more important is the dramatic pH changes in water as it moves off-site. Metal solubility is a function of solution pH. Any change in pH will effect metal concentrations. As AMD moves off-site, other water quality constituents are picked up and as pH increases and alkalinity and hardness increase metal concentrations decrease.

Geology appears to be the strongest determinant of water quality as effected by hard rock mining in defining initial source waters (Plumlee et al., 1994). Geology has also been used as a determinant of overall water quality (Hem, 1990).

Metal sorption onto suspended particulates may control metal mobility from mine sites and weathering mineral deposits (Smith et al., 1992; 1993). The amounts of metals sorbed depend on the amount of suspended particulate; pH of the waters; and the speciation and concentration of the metals in the drainage waters (Plumlee et al., 1994).

Given the most significant influence of hard rock mining on water quality is AMD generation, and AMD volumes are low, regional characterization of water quality is difficult. Again the variability in water quality and the lack of definition of the mining activities in relation to streamflow routing processes precludes a regional water quality model.

Further, water quality sampling for heavy metals presents a series of problems and issues that are addressed in the next section.

Water Quality Sampling for Metals

Water filtered through a 0.45 μ m membrane filter and acidified with ultrapure nitric acid to a pH less than 2, represents the 'dissolved' fraction. The dissolved fraction is bioavailable. Sample collection and filtration are usually done in the field. The unfiltered sample is also acidified and represents the total fraction. The total metal analysis may or may not include an acid digestion, with or without heat. The total sample represents the dissolved metal plus the part that is solubilized from the suspended solids (inorganic and organic) in the sample by the mineral acid employed as a preservative.

Water quality standards (promulgated) on water quality criteria (recommendations) can only be developed for metal (and often other water quality parameters) when the toxicological effects on human, aquatic, and terrestrial life forms are known. The chemical and physical forms of the expected constituent must be known to properly determine any threshold of concern. These forms may vary with varying environmental conditions and hence toxicity may vary over environmental space and/or time. Further, metal standards may vary by individual life form (species), life form age, and with other constituents present exhibit additive, synergistic or antagonistic interactions. This is a very complex problem that has only recently been addressed. This section of the review will present a generic review of metal forms and their toxicity in the aquatic environment.

In the aquatic environment metals can be found in the following phases:

- 1) dissolved as free ions and complexes

- 2) particulates; inorganic precipitates or sorbed with organic compounds or clay particles
- 3) sorbed or mixed with stream bottom sediments
- 4) sorbed or incorporated into living biomass

Dissolved Phase

Trace metals can be present as free ions, soluble carbonates, sulphides, hydroxides, chloride or sulphate complexes, and soluble complexes with organic ligands (Morel et al., 1973). Calculations in other model studies have also included precipitation and adsorption (Morgan and Vuceta, 1976).

Although typically the concentration of metal ions in the dissolved phase is low compared with the suspended or colloidal particles, in many cases the greatest quantity of each element, sometimes over 90%, occurs in the dissolved phase simply because the dissolved solids comprise a large percentage of the total solids (Perhac 1974). Exceptions to this rule are iron and manganese, which are major constituents of both suspended and colloidal particles.

Laboratory experiments on the toxicity of lead to rainbow trout showed that the results could be interpreted only in relation to the concentration of the dissolved lead measured by pulsed polarography. The results for the "total" (dissolved plus colloidal) measured by atomic absorption became less indicative as the increased alkalinity (or hardness) reduced the solubility of the lead by forming precipitates and colloidal particles (Davies 1976). The toxicity of lead correlated well with the dissolved lead concentration but not with that of "total", defined in this case as dissolved plus colloidal lead. Apparently a series of antagonistic reactions of calcium and/or hardness and complexation occurred in water, rendering a certain fraction of the "total" lead concentration nontoxic. In long-term toxicity tests, the "no-effect" concentration occurred

between 18.2 ug/L and 31.6 ug/L dissolved lead. The corresponding “total” lead concentrations were 120 ug/L and 360 ug/L, respectively (Davies, 1976).

The Influence of Ligands and Complexation on Metals

In general, organic complexation reduced the biological availability of trace metals in solution compared with their inorganic forms (Jenne and Luoma, 1977). The toxicity of copper and zinc to juvenile Atlantic salmon was reduced by the presence of humic acids (Cook and Cote, 1972). Similar results were obtained in experiments conducted with guppies; the toxicity of copper was reduced in the presence of NTA, EDTA, humic acid and glycine (Chynoweth et al., 1976).

Model calculations have shown that in fresh waters the complexation of metals with humic materials depends on (a) the pH which controls the competition from carbonate and hydroxy ligands; (b) the major ions concentrations, e.g., calcium and magnesium ions are competing with the trace metals for humic materials and chloro and sulphato ligands are competing with humic materials for trace metals; and (c) the stability constant of the metal-humic interaction with humic substances for natural environments showing a wide range of values of their stability constants with any particular metal (Mantoura et al., 1978).

The filtering procedure is subject to criticism for not providing an accurate appraisal of total heavy metals present in the water column. The unfiltered samples give a more reliable indication of the amounts of heavy metals transported by the stream, but accurate estimates will probably require sediment and biological profiles (Gale et al., 1973).

Metals Associated with Suspended Materials

Metals are found in natural waters associated with suspended particulate matter. Sometimes the majority of the particles are hydrous metal oxides such as those of Fe(III) and Mn(IV). It seems likely that hydrous oxide coatings are partly developed during weathering, pedogenesis and transport of terrigenous material downriver (Grieve and Fletcher, 1976). Metals can adsorb on these metal oxides and on clay particles or can be found in association with large-size organic molecules. The bonding can be by electrostatic attraction or chemical coordination. At the normal pH of natural waters (6.5 to 8.5), a variety of inorganic solids prevalent in natural waters such as Fe_3O_4 , $\text{Al}(\text{OH})_3$, MnO , SiO_2 and kaolinite is negatively charged, thus exhibiting an electrostatic attraction for metal cations (Stumm and Morgan, 1970). At pH >6 Cu was completely removed from solution (Payne and Pickering, 1976). At pH <5 protons successfully competed for adsorption sites, and at pH <3.5, no Cu ion uptake occurred. The addition of various ligands changed this situation completely. At pH <5 the presence of the ligands led to an increased copper adsorption. At higher pH levels some ligands (tartrate and gluconate) limited the amount of copper sorbed by the clay suspension. Similarly, when the ligand was in contact with the clay prior to the addition of copper ions, the amount of copper taken up was reduced. On the other hand, no adsorption occurred when clay was added to a solution containing preformed complex.

In another study it was found that 50% to 80% of the total copper present in river waters was in the suspended solids phase, possibly as oxide, sulphide and malachite precipitates adsorbed on clay particles or complexed by organic molecules. The removal of copper from the solution was fast. From a solution containing 0.8 mg/L copper, 75% of the copper was removed in two

hours (Montgomery and Stiff, 1971). Lead concentrations in filtered (0.45 μ m) water ranged from nondetectable to 15 μ g/L, but from 15 μ g/L to 200 μ g/L in the suspended solids in Saline Branch (Getz et al., 1977). Potentially, the ratio of dissolved metal concentrations to total metal concentrations may be used to characterize water quality. The ratio of dissolved metal concentration (0.45 μ m) to the total fractions ranged from 0.1 for iron to 2.7 for cadmium (Romano et al., 1977). Similar ratios, approximately 0.4 for copper and iron and 4 for zinc, were found in the River Hayle, Cornwall (Brown, 1977).

The situation seems to be different in the case of mercury. In a study of the Kuskokwim River, Alaska, situated near cinnabar (HgS) deposits, the geometric mean concentration of mercury in the suspended materials was 3.9 mg/kg, while the corresponding concentration in water was 0.34 μ g/L (Nelson et al., 1977). Considering the discharge of the river, however, it was calculated that 80% of the mercury was transported by water, 19% by the suspended materials and the rest by the bottom sediments. This was in agreement with the results obtained for the Ottawa River (Miller and Laham, 1976). In this case, 87.3% of the mercury was transported by water, 9.5% by the suspended sediments and 3.2% by the bottom sediments.

In tests with zinc and copper solutions prepared in the laboratory it was shown that the toxicity to fish of a given concentration of the metal ion decreased as the concentration of added suspended solids increased. The suspended solids added consisted of humus tank solids from a sewage plant which treats a detergent-free domestic sewage. If the copper was measured as "soluble" (defined as that passing through a 0.45 μ m average pore size membrane filter), then the toxicity to fish increased with increased concentrations of suspended solids. The added suspended solids did not affect the toxicity of nickel and increased the toxicity of cadmium by a

factor of four. The concentration of the soluble zinc, copper and cadmium fell quickly after the preparation of the solids-metal-salt-solution mixture. The decay rate was pH dependent (Brown, 1976).

Metals Associated with Bottom Materials

Sediment plays an important role in water quality. Part of the assimilative capacity of natural water systems for metals, pesticides and herbicides is the ability of the sediment to bind these substances, thus removing them from the water. On the other hand, many toxic substances stored in the sediment are released to the surrounding waters by a variety of chemical and biochemical reactions, thus making them available to the organisms living in these waters. Lake and stream sediments often reflect recent additions of heavy metals before elevations of such elements are detectable in the overlying water (Stokes and Szokalo, 1977). The possibility of reentry of sedimented material into the water, due to physical, chemical, or biological processes in natural situations, always exists. Also, with bottom feeding fish, sediments may be more important than water as a source of heavy metals (Florence and Batley, 1977).

The biological availability of any metal from the sediment depends on a series of variables such as the chemical form of the metal and the chemical composition, crystallinity, surface area, coating and mineralogy of the sediment. The physical and chemical characteristics of the associated water are also important in determining the biological availability of trace metals from sediment particles because of the direct role the water plays in the sorption and dissolution processes (Jenne and Luoma, 1977). Substantial frequencies of mortality and teratogenesis occurred when eggs of the narrow-mouthed toad, goldfish and rainbow trout were cultured in contaminant-free water added to natural sediments containing average concentrations of

0.052 mg/kg mercury, 1.0 mg/kg cadmium and 108.2 mg/kg zinc. The sediments were more lethal to eggs and embryos than to free-living larvae or fry. Survival of trout embryos and alevins paralleled sediment concentrations (Birge et al., 1977).

The transfer of metals between bottom materials and the water above them is a complex process depending on a multitude of factors such as the oxygen concentration (aerobic or anaerobic conditions), the nature and the concentration of heavy metals and the organic and inorganic ligands present, the pH, and the particle size of the bottom sediments (Lee and Mariani, 1977; Lu and Chen, 1977). Some of the individual processes that may be involved in this transfer are surface exchange, diffusion exchange, precipitation, coprecipitation, complexation and dissolution (Jenne and Luoma, 1977). Another transfer mechanism from bottom mud sediments to water proposed for lead is that aquatic plants absorb lead through the root system and subsequently the lead is released into the water from the decaying leaves (Welsh and Denny, 1976).

Iron and manganese oxides act as a sink for trace metals (Co, Ni, Cu and Zn) (Jenne, 1966; Lee, 1975). The various degrees of sorptive activity of the oxides depended, among other things, on their age. The nonstoichiometry of the reactions between the hydrous metal oxides and the metals made simple solution equilibria and chemical kinetics inapplicable to these systems. Manganese dioxide also had a strong sorptive capacity for silver (Boyle, 1968).

Experimental results have shown that clay materials can remove lead from solution. The process can be reversed by a sudden decrease in pH or by a change in the ionic composition of the solution. Di- and trivalent ions compete with lead and may exchange with it, thus permitted lead to come into solution (Griffin and Shimp, 1976).

Adsorption of metals onto hydrous oxides and soils increased abruptly at pH 5 to 6 for Cu, Pb and Zn, and at pH 6 to 7 for cadmium. In the presence of anions, adsorption of heavy metals was more pronounced. Anions enhanced heavy metal adsorption at low pH values when adsorption was not likely to occur in their absence (Huang et al., 1977).

The concentration of metals in bottom sediments is generally much higher than in the overlying waters. Concentration factors ranging from approximately 400 to 4000 were found for a series of metals in a study of the Susquehanna River ecosystem in New York State (McDuffie et al., 1976). Confirming other observations, the same study found that the total metal concentrations increased as the particle size decreased. The average ratio of metal concentration in the silt plus clay to sand fraction ranged from 4.3 for manganese to 23.1 for silver. In the overall transport 10% to 24% of the metals were carried in the silt fraction, 21% to 35% in the clay fraction, and only 1% to 2% in the sand fraction. As mentioned before, the rest (38% to 63%) was carried in the dissolved phase (0.45 μ m). The study of the Kuskokwim River mentioned previously (Nelson et al., 1977) showed that the mercury concentration in the finest size fraction (<0.062 mm) of bottom materials was much higher than in the coarse fraction (>0.25 mm). The respective concentrations ranged from approximately 1 mg/kg to 35 mg/kg and from 0.1 mg/kg to 2 mg/kg. The dispersal distance of the finer sized sediments was also greater. The general trend of increased metal concentration with decreasing grain size (Delisle et al., (1975); Perhac, 1974). Surface adsorption phenomena might be a prime factor in controlling metal distribution in bottom sediments. Calcium and manganese were exceptions to this rule; their concentration increased with increased particle size. Apparently NH_4OAc extracts the surface-sorbed cations, thus giving an indication of the exchangeable metal content. Metal concentration

in the sediments are related to the surface area of the variously sized particles. The metal concentrations (Cu, Pb, Ni, Co, Fe, Mn, Cr) in the sediments from the Ottawa and Rideau rivers significantly correlated with the surface area of the sediment fraction (Oliver, 1973).

Strong negative correlations were found between the concentration of Co, Cu, Fe, Mn, Pb and Zn in the minus 80-mesh fraction of the sediments from the Fraser River delta and the percentage of sand (>270 mesh) in the same fraction (Grieve and Fletcher, 1976) and between Cu, Zn, Cd, Cr, Ni and Hg concentrations and the sand (mean grain size, 118 μm) content of bottom sediment samples collected at the mouth of the Fox River in Wisconsin (Pezzetta and Iskander, 1975). At the same time positive correlations were found between the same metals and the silt (mean grain size, 21.5 μm) content of the sediment samples. Similarly, strong negative correlations were found between both detrital (acid insoluble) and nondetrital metal (Cu, Zn and Pb) content and the silt (53-2000 μm) content in the sediment of the Saguenay fjord. Strong positive correlations were found between the same metals and the mud content (<53 μm). Most of the metal content (>75%) was found in the detrital fraction of the sediment (Loring, 1976). "Natural" background concentrations were distinguished from polluted conditions for Cr, Cu, Pb and Zn in the bottom sediments of the Willamette River in Oregon by analyzing the <20 μm fraction of the sediments (Rickert et al., 1977). The sediment fraction of <2 μm is a good pollution indicator (Wittman and Forstner, 1976).

There is no clear indication from the literature of which species should be monitored in the aquatic environment to ensure that the toxic effects of various pollutants are properly assessed. Several analytical schemes have been proposed to separate various metal fractions, however universal acceptance is not forthcoming. Recently a large water conservancy district in the

southeastern United States and the U.S. Geological Survey proposed the operational definition of dissolved metals as being that which passes through a 0.1 micron filter.

Recent work by our lab suggests that dissolved metal concentration measurements may be an artifact of water filter size, filter composition, and filtration type (vacuum or pressure).

Additional research is needed to better define dissolved metal concentrations in water samples.

The toxic effects of metals vary depending upon the metal and the level and duration of the dose or exposure. Toxic effects may be seen almost immediately following large doses of short duration - acute effects. Alternatively, the effects may be subtle in their appearance and noticeable after long exposure to low doses - chronic effects. All toxic metals are capable of causing both acute and chronic effects.

SUMMARY

This objective was to review the literature on the effects of different mining operations on water quality, ranging from sand and gravel to precious metals. In general, site disturbance is the one common theme in any mining operation. This site disturbance may result in increased soil erosion and subsequent suspended sediment increases in surface waters. Chemical effects from mining operations are varied between resource types, mining activity, and geographic location. A set of recommended water quality monitoring parameters was suggested for each resource type. This parameter list is not meant to be exhaustive, rather to be used as a guidance document. Significant differences exist in heavy metal sampling and analytical protocols. Additional work is recommended in this area.

Many studies have been published documenting the effects of specific mining activities on water quantity and water quality in the United States. Most studies tend to be basin specific and look at above - below or mined - unmined comparisons only. Studies that assessed the effect of mining activities over time and space are rare. It was indeterminate if so few studies assess water quality changes downstream at several points below a mining activity because no such studies are done, water quality differences are not significant further downstream or are measurable downstream, or if additional land use activities compound the interpretation of the water quality results. Individual studies on individual mining operations can and do document water quality effects - significant or not. We found no studies that assessed mining activities basin-wide.

All mining operations are not the same. Abandoned mine sites may influence water quality more than any active mine site. All mines do not contribute equally or proportionately to the water balance. Acid mine drainage in headwater streams may be significant onsite, but

downstream dilution, pH changes and metals mobility decreases mask cumulative effects. Further work in this area is suggested.

Water quality models have been developed for various mining effects assessments. Large scale data compilations and synthesis of regional water quality relations have had none to little success. The more successful regional compilations of water quality data tended to include a specific geologic information and data and either site specific or extensive water quality monitoring data. The literature review suggest that the streamflow generating mechanisms are important determinants for mine water quality. These determinants are not easily accessible from the existing databases. Regional analysis of water quality as effected by mining operations will require significant additional data collection. The success of a regional analysis is still uncertain.

The regulatory requirement that runoff waters be captured and treated from all reclaimed areas regardless of ambient conditions has been found to be unjustified in the arid southwest United States (Kiefer and Balzer, 1981). The importance of baseline water quality and quantity cannot be overstated (i.e., Driver and Williams, 1991).

Mine operations permitting is regulated at the state level, with state legislation that parallels the federal mandates. Mine permit applications are required to address potential cumulative impacts and to assure the permitting authority that water quality standards will be met under normal operating conditions. The determination of these impacts is far from straight forward (Betson, 1982). The time frame associated with the review of mine permit applications does not allow for extensive collections of water quantity and quality data once a permit has been requested (Kostelnik and Witt, 1989). Therefore water quality data bases need to be established.

Basin

complexity, geology and previous land uses must be considered to improve water quality data interpretation (Kostelnik and Durlin, 1989). Ore type and geologic deposit information are usually confidential and may or may not help water quality characterization.

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Objective 2. Summarize the findings of case studies on the effects of mining activities on water quality.

The purpose of this objective was to summarize the findings of case studies on the effects of mining activities on water quality as reviewed in Objective 1. Compilation of literature on the effects of mining on water quality was relatively easy. Most of the literature was case studies documenting the influence of a single mining activity on water quality, usually on-site. Very few studies addressed off-site (downstream) water quality changes as influenced by the mining activities.

The synthesis of the literature into an understanding of the larger watershed scale or universal processes affecting water quality was unsuccessful. Is a large watershed scale spatial or statistical analysis on the influences on mining activities on water quality achievable?

We attempted to relate water quality data (downloaded from the U.S. Geological Survey) to mining activities, but found that the water quality data were too variable to allow for correlation to mining activities. Water quality sampling frequency and parameters tested varied by station. Water quality data common to all stations were evaluated for correlation to metal concentrations, since metal concentrations were considered the best indicator of mining influences on water quality. Metal concentrations (either as dissolved or total) were not correlated to any major water quality constituent. Constituents evaluated included: sulfate, bicarbonate, alkalinity, hardness and pH. Other major constituents were not evaluated since no causal mechanisms were implied.

Water quality data were analyzed by correlation coefficients to determine potential linkages to mining activities. Water quality data were often variable in time and space, and

furthermore water quality parameters often changed with sampling location, including major cations and anions, as well as heavy metal concentrations. Heavy metal data were often skewed because of sample analyses reported below detection, thus the median value was used as a definition of the central tendency. The Upper Arkansas River Basin and the San Juan River Basin have past mining activities, current water quality issues related to mining, and are both familiar to the study team. We looked at changes in metal concentrations over time (Arkansas) and over space (San Juan).

During the summer of 1977, two undergraduate students in the Research Experience for Undergraduates (REU) funded by the National Science Foundation each examined a Colorado river basin impacted by mining activities and/or acid mine drainage.

The first study was in the Upper Arkansas River Basin. The headwaters have long been subjected to acid mine drainage. Two water treatment plants began treatment of acid mine drainage waters in 1992.

Water quality data were compared between the pre-treatment and post-treatment time periods at eight different sampling locations. The eight sampling stations are operated by the U.S. Geological Survey. Water quality parameters tested at each site changed over time, including heavy metals. Ostensibly metal concentrations would decrease with distance downstream and after treatment implementation. In general, heavy metal concentrations (both dissolved and total) decreased with time, but did not decrease with downstream distance.

Has Treatment Decreased Heavy Metal Load in the Upper Arkansas River ?

by William N. Folsom



Introduction

The headwaters of the Upper Arkansas river originate around Leadville Colorado, located in the central part of the state. Leadville, which is south of Denver, has been an active mining center for over 100 years. Oro city camp, the first mining center, was established in 1860. The gold vein that was discovered there dwindled, but another boom occurred with the discovery of lead and silver deposits. When the price of silver declined in 1893 Leadville's economy also declined until the 1930's when a use for molybdenum was discovered.(Albertson, 1997) Mining has continued in the basin and is still a major factor affecting the water quality of the region. General water quality can be affected by many other factors such as trans mountain diversions , direct runoff , and water use. (Clark, 1997) However, this report will focus on mine drainage and its treatment.

The Upper Arkansas is a semi arid basin that drains 4,670 square miles. The major hydrological inputs are precipitation and trans mountain flows. The Arkansas river has an elevation drop of 6,750 feet from Leadville to Canon City. This is about 100 miles. The entire reach of the Arkansas drains one quarter of the state of Colorado. It is the largest drainage in the state and important to water users.

This report will attempt to quantify the change in heavy metal load of the Upper Arkansas since the implementation of two acid mine drainage treatment plants in March, 1992. In recent studies concentration has been the focus when examining heavy metals and water quality. This may be somewhat quantify able, but one might ask, "How much load is actually in the river at a given time, and, is it lower further down stream from treatment?"

Acid Mine Drainage, Heavy Metals, and Treatment

Most precious metal deposits are complexed with other metals and are contained in sulfide deposits. The mining process increases the exposure of metal sulfides to oxygen and water and greatly accelerates the natural acid producing process. This mobilizes the metals in the deposits and they can enter receiving streams in higher concentrations than in a natural system. (Wentz, 1972) The water quality in the basin has historically been altered by this process.

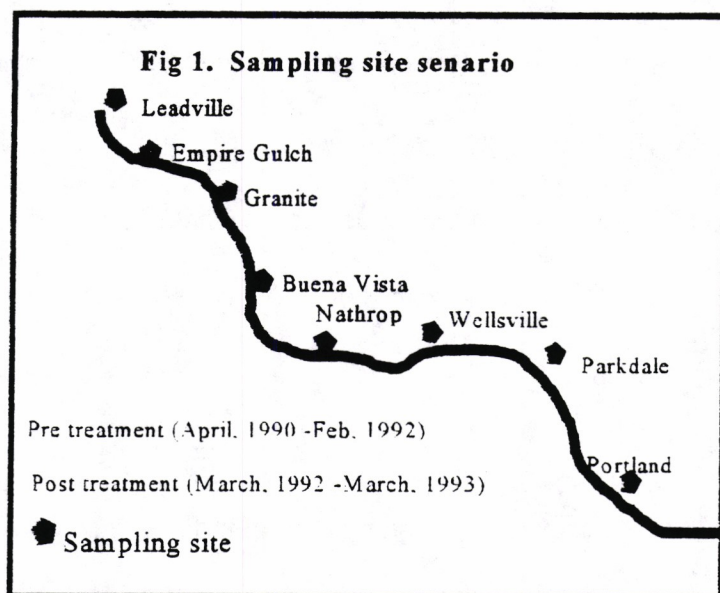
Water quality between Leadville and Pueblo has been substantially degraded by mining activity. Water flows through tailings piles, primarily in the Leadville area and has contributed to high concentrations of cadmium, copper, manganese, zinc and other elements in the river. This is important because acid mine drainage has historically been toxic to biota in the river, especially affected are brown trout .

In the spring of 1992, after years of study of two major point sources, by the Environmental Protection Agency (EPA), and by record of decision, two treatment plants came on line. The A.S.A.R.C.O mining company operates the Yak Tunnel treatment facility, and the Bureau of Reclamation (BR) operates the Leadville Mine Drainage Plant. Both facilities are very efficient in the removal of heavy metals from it's influent. The Yak discharges treated water into California Gulch which runs into the Arkansas just south of Leadville. The Leadville Drainage Plant discharges into the East Fork. Both the BR and A.S.A.R.C.O claim high success in cleaning up the Arkansas.

Methods of Study

The data used for this study is documented by the U.S.G.S in 1990 in a report done in cooperation with local agencies by Dash and Ortiz. This data was useful for this report because it included instantaneous discharge rates with the metals data needed. This data covers the period, April, 1990 - March, 1993. (Dash, 1996) During this period, 207 water samples were collected from eight sites on the upper Arkansas river

between Leadville and Portland. This data was then separated into two periods, pre-treatment and post-treatment. The pre-treatment period runs from April, 1990 - February 1992. The post-treatment period covers March, 1992 - March 1993. Metals data is reported in micrograms per liter and discharge rates in cubic feet per second. This



data was then converted into load by the use of a simple conversion equation. The result of the equation $:[u/l * cfs * K]$ (K= conversion factors), yields the load on the river in Kg/day at the time of sampling. Statistical analysis was then run on the load of each metal, at each station, for each sampling, during each period. These results were skewed so the median values were used. The results of this process are illustrated in graph form. (Figures 2 - 7)

Results

Cadmium

The results of the data show significant decreases in load, but also increases. Dissolved cadmium, (under 45 micrograms), has decreased at all stations while there have been some increases in Wellsville and Parkdale in total levels.(Fig2.)

Copper

Copper load changes, illustrated in figure 3, show significant decreases in its total form. The dissolved constituent increases from the granite station to the end of the study reach.

Lead (Figure 4)

Decreases are prevalent from Leadville to Parkdale in total levels, with increases in dissolved lead. The difference in lead is higher between dissolved levels and total levels.

Manganese

The change in Manganese over the two periods indicates more decreases in dissolved levels than the previous charts. Some increases are to be noted regarding the south part of the reach.(fig 5)

Fig 2. Change in Cadmium pre - post treatment

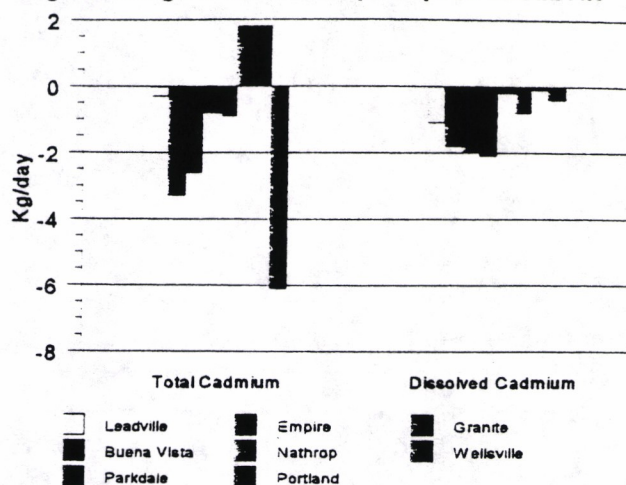
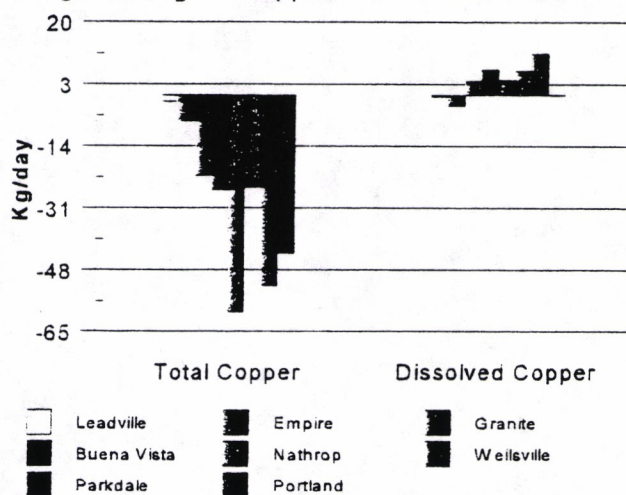
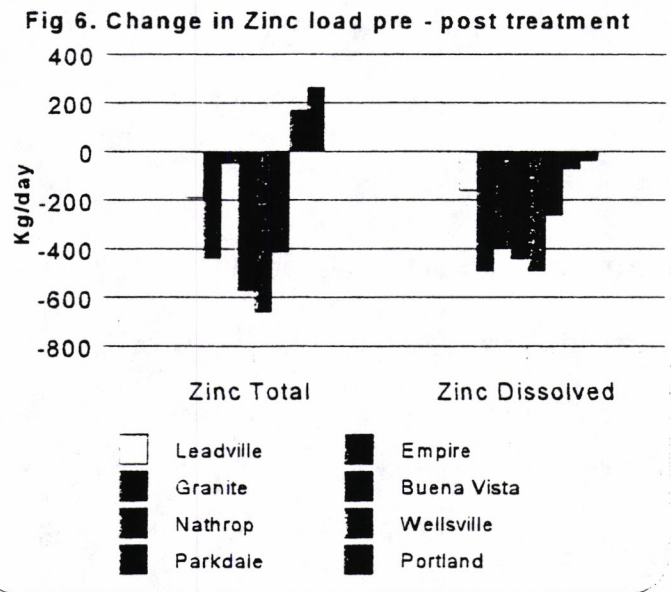
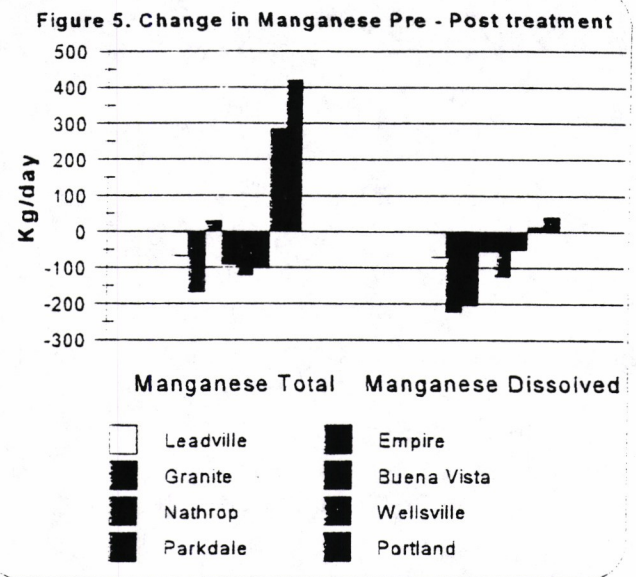
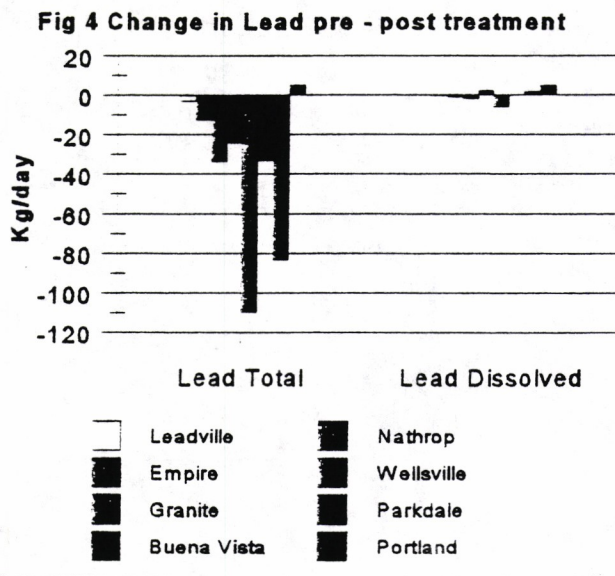


Fig 3. Change in Copper Pre - Post treatment

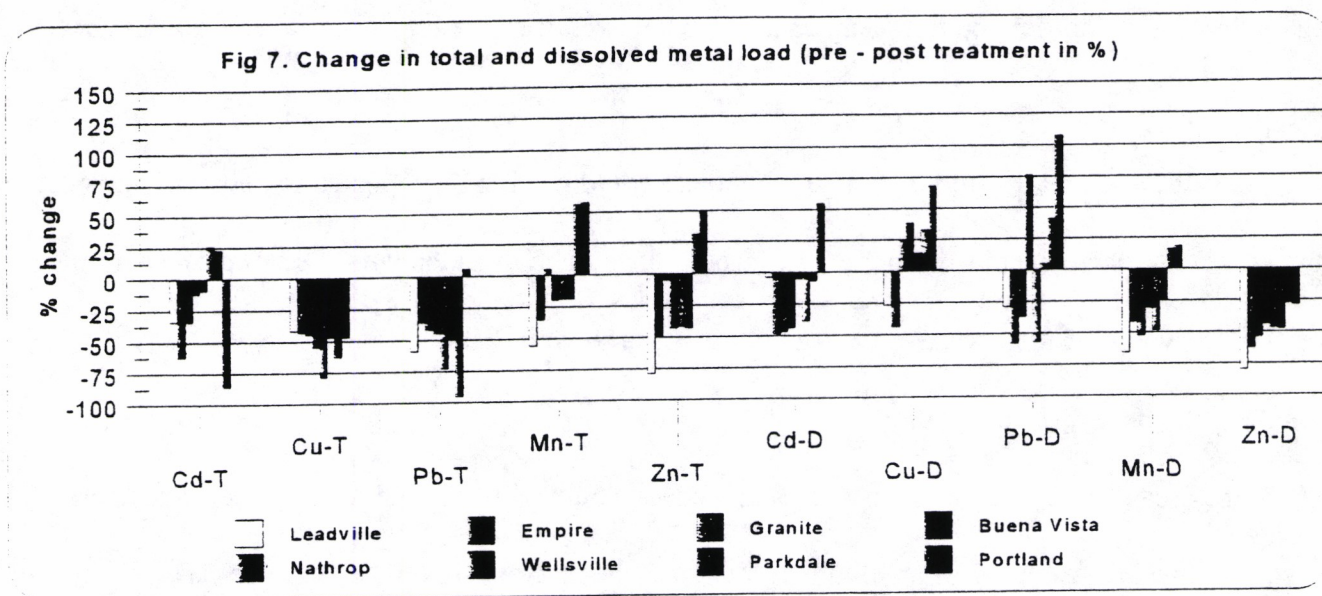




Zinc

Figure 6 illustrates a significant decrease in both total and dissolved load. Increases are to be noted in Parkdale and Portland.

Figure 7 presents all changes in load in a percentage. It can be seen that the decreases out weigh the increases. A quantity measurement in load along the entire reach is not shown and was not calculated because it would not compute to run another analysis on median values.



Discussion

It has long been documented that metals can take many pathways in the environment and that their movement is related to stream flow regimes.(Clark, 1996) It can be expected that dissolved metals will move further downstream while larger particles may have more variability in movement . This perhaps is evidenced in Figure 7 for dissolved zinc. We know for instance that the removal success is about 99% for zinc. This may be shown in the above graph as the decrease levels are also high and there seems to be a spacial relationship as the metal moves downstream. It is difficult to examine the movements of metals with this data because there isn't enough of it.

Conclusions

There has been a significant decrease in heavy metal load along the upper reach of the Arkansas river from pre to post treatment. Although a change can be noted, it is hard to quantify that change. Statistical analysis yielded a high degree of skewness in data and the best measure of central tendency was median values. Building on this to try to quantify an overall figure for the entire reach would not be accurate.

To continue this study more water quality data would need to be collected to help with the post treatment period. Instantaneous discharge rates would have to be included with the samples taken. In any undertaking it would be ideal to have the right kind and amount of data needed, however this is not always possible in real world situations.

Some areas of the river show increases in load. It would be beneficial to learn more about any land use activities, flow events, or anything else that may be responsible for the increases. The Twin Lakes system may be an area to consider in a follow up study as well as activities further down stream. It may also be wise to gather information regarding the biota in the river. Certainly changes in fish and macro invertebrate populations may be good indicators to river health. In summary, the data collected yielded good results regarding decreased load on the river. However follow up studies that include more watershed variables may be beneficial.

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The second REU study looked at metal concentrations and metal loads in the San Juan River Basin. The area has long been subject to mining influences on water quality, and no remediation has been done on the metal sources. Metal loads were not a function of tributary source loads only. Metal loads (and concentrations) were not related to mine location.

Characterization of Heavy Metals in the San Juan River

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July 25, 1997

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Advised by:

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Funded by:

The National Science Foundation

Abstract:

Mining in the area around the San Juan River Basin has exposed the river and surrounding waters to metal contaminants. Unlike the headwaters of the Arkansas River the San Juan and its tributaries remain largely unreclaimed. This study takes water quality data from the US Geological Survey to attempt to characterize the metal concentrations and loads along the San Juan River.

Water quality data was taken for the main USGS stations along the river and the farthest station downstream on its tributaries. Statistical central tendencies were used to compute yearly concentrations and loads for both dissolved and total metals. These yearly values were then averaged to obtain a typical value for each constituent at each station along the river. The metals of interest were arsenic, copper, cadmium, lead, manganese, molybdenum, and lead. These results were represented with charts and tables depicting the values.

This report include graphs of the concentrations and loads by station, maps of the system overlaid with mine locations and metal concentrations and yearly values for the metals. The river proved too complex for this analysis. No solid relation was seen between the location of mines and the metal concentrations. Furthermore the metal loads along the river were not a simple sum of the inflows from the tributaries. Further studies of smaller areas may yield better results and a more coherent picture.

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1.0 INTRODUCTION

Historic mining activity left a vast legacy of stories, towns, families, and traditions. Unfortunately the mining days also left a source of heavy metal contamination. Byproducts of the mining industry such as tailings piles and mine dewatering tunnels frequently lie in or nearby streams. Water flowing down the watershed can leech out the metals and move them downstream causing fish kills, ecological damage, and impairing the use of water for human activities. The metals transport in two main forms, as a dissolved constituent or a solid. Dissolved particles are able to pass through a 45 micron filter while solids remain trapped. The dissolved state poses a greater risk to a town or ecosystem due to greater bioavailability. The state of the metal and the toxicity depends upon the properties of the water such as pH, alkalinity and hardness. Lower pHs push metals toward the dissolved state; alkalinity and hardness effect the toxicity by forming complexes which bind the metals. The elemental form of a metal typically is the most hazardous. Metals do not remain in a static state as a dissolved or solid particle or even as a complex or free element. A metal may pass harmlessly through one system in one form only to transform under different conditions downstream and cause damage.

The headwaters of the Arkansas river around Leadville undergo some treatment and renovation to attempt to solve the metal pollution problem. In contrast the San Juan River remains largely unreclaimed. This study examined the metal concentration and loads along the length of the San Juan River to characterize the metals and possibly suggest a treatment strategy. For many years the US Geological Survey (USGS) has monitored water quality parameters for main watersheds, including the San Juan river. The USGS historic data for the San Juan was used to paint a picture representing the state of the river. High concentrations of metals were expected at the confluence of streams subjected to heavy mining activity with a dilution effect as the waters hit the main stem. The loads moving down the river were expected to increase as a sum of the sources from the tributaries. Unfortunately the system proved to complex and too large to define a quantitative relation between the stations and the different constituents. Several qualitative conclusions were drawn debunking the expectations and a smaller area for a more focused study is recommended for future work.

2.0 METHODS

2.1 SOURCE AND SCOPE OF DATA

Historic water quality data for the entire length of the San Juan river was obtained from United States Geological Survey (USGS) through Earth Info's Quality of Water 1996 CD-ROM. The initial records examine began in 1950 and continued up to the most recent information found on the CD, typically the late 1980s. The majority of the metal records did not start until 1969 so earlier data was discarded. The total and dissolved concentrations were examined for arsenic, cadmium, copper, lead, manganese, molybdenum, and zinc. In addition; discharge, pH, sulfate, temperature, alkalinity, hardness, specific conductance, and sediment loads were also included in the analysis. For the purpose of statistical study all values recorded as a non-detect were treated as 70% of the detection limit.

2.2 ANALYSIS STRATEGY

The available data fell short of the ideal statistical sample with differing sample dates and gaps in the record. Compensating for the shortcomings to generate a meaningful result became an iterative process with a variety of techniques attempted. Microsoft Excel was programmed to sort the data and perform all statistical calculations.

The first analysis consisted of averaging the different values of the constituents over all available years at each station along the river. The changes in the individual constituents from station to station did not show a pattern, so a more detailed approach was attempted. Mine locations were researched to try and determine the location of the sources. Classification of land use and diversions was initially attempted but proved too involved for the scope of this study. The second analysis also expanded to include major tributaries at the USGS station closest to the San Juan. Figure 1 shows the different stations and their locations along the basin. Stations on the main river are shaded.

2.3 STATISTICAL AND NUMERICAL MANIPULATION AND REPORTING

Each constituent at each station was summarized into yearly values by taking the central tendency for each year. The central tendency was the average in the case of a normal distribution and the median in the case of a non-normal distribution. Sets with an absolute value of the skewness less than one were summarized as the mean. Sets with skewness values greater

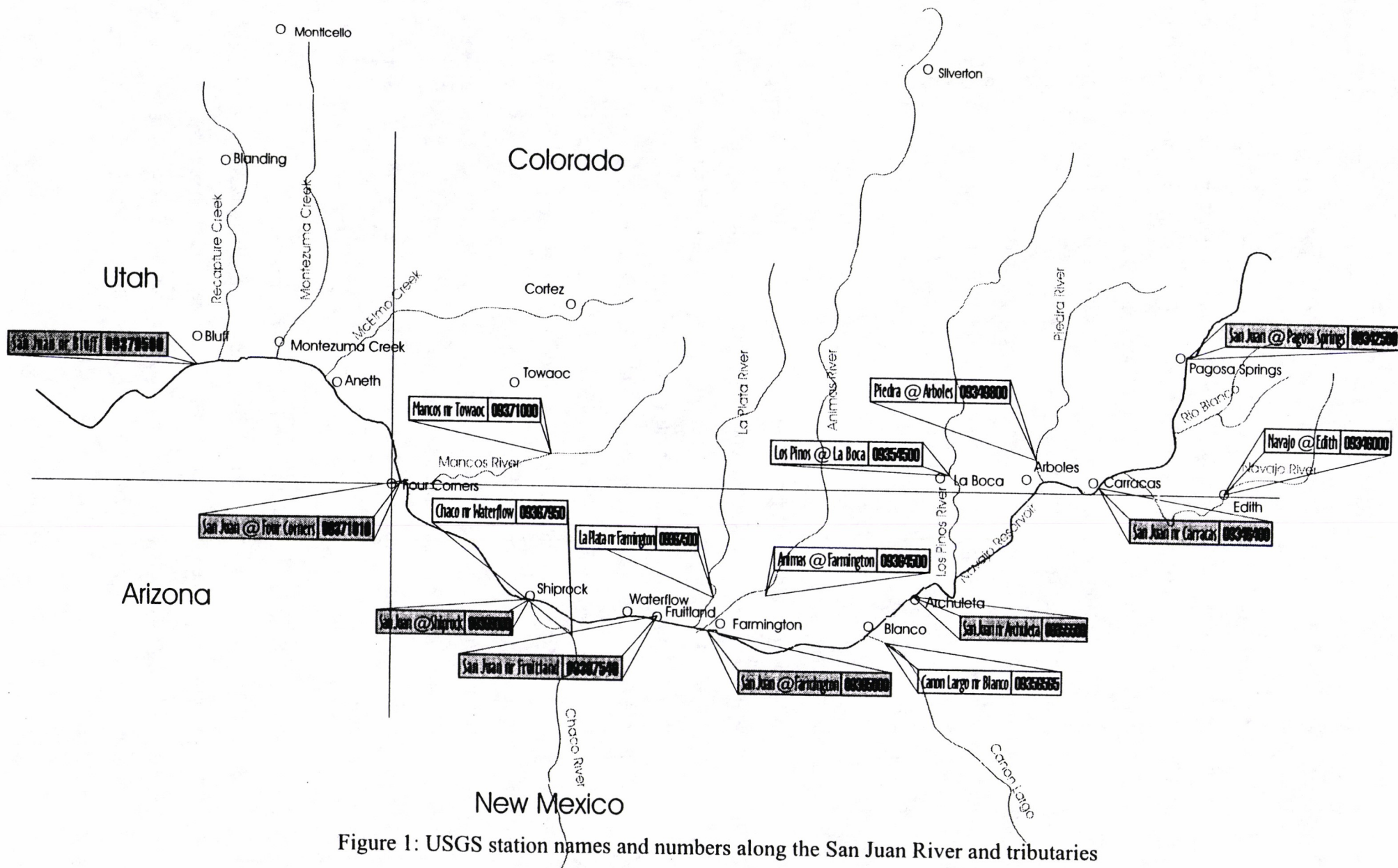


Figure 1: USGS station names and numbers along the San Juan River and tributaries

than one were summarized as the median. Years with no values were left blank. Years with one value present were classified by that number. Years with two values were averaged. These yearly central tendencies were used, in combination with the central tendency of the discharge for the year, to compute a yearly total and dissolved load for each metal. The central tendency of all the years for each constituent was then computed to determine the typical metal load or concentration at each station along the river.

2.4 METHODS FOR INTERPRETATION

To detect trends, the dissolved and total loads and concentrations were plotted by station. A map of the site was digitized and the metal loads of the main stem and the tributaries were compared to see the relationship between the tributary influxes and the metals in the main river. The location of major mines was overlaid onto the map to attempt to connect the location of major mines with the loads. The lack of pattern in the second analysis prompted several other attempts to make sense of the data. Ratios between the dissolved and total concentrations were examined. A correlation was attempted between discharge and concentration to try to fill in gaps in the record through regression. To see if outlying values were significantly effecting the results the station at Shiprock was chosen to analyze in detail since it had the largest and most complete record. Outlying values were discarded and replaced with the mean and correlation calculations were run. This procedure was repeated for all metals several times until the data set was determined to be way past ethically reasonable manipulation. A large table of correlations between all water quality properties was run to check for correlations. Several indexing attempts were made using non-metallic properties and relations between the metals. Upon failure of all these attempts the decision was made that the system was too complex for this analysis to explain and the data can show the metal concentrations but not the rational behind the values.

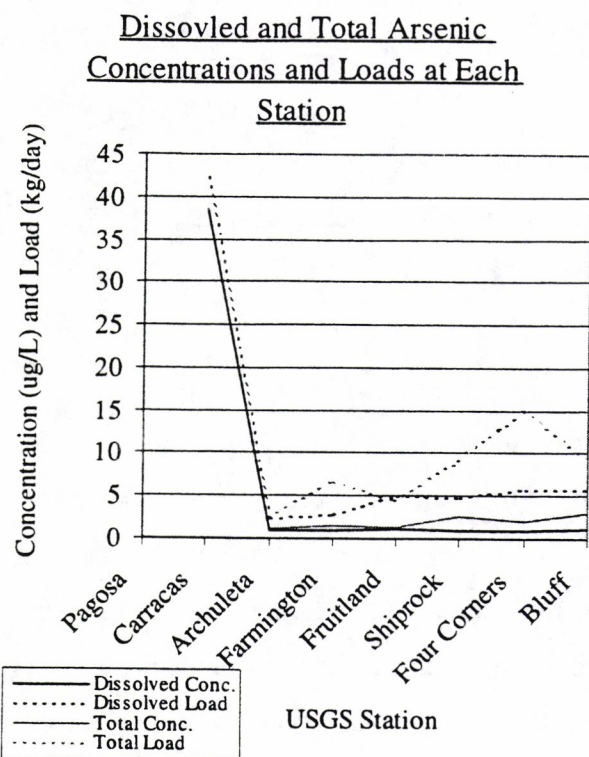


Figure 2: Dissolved and total arsenic concentrations and loads along the San Juan.

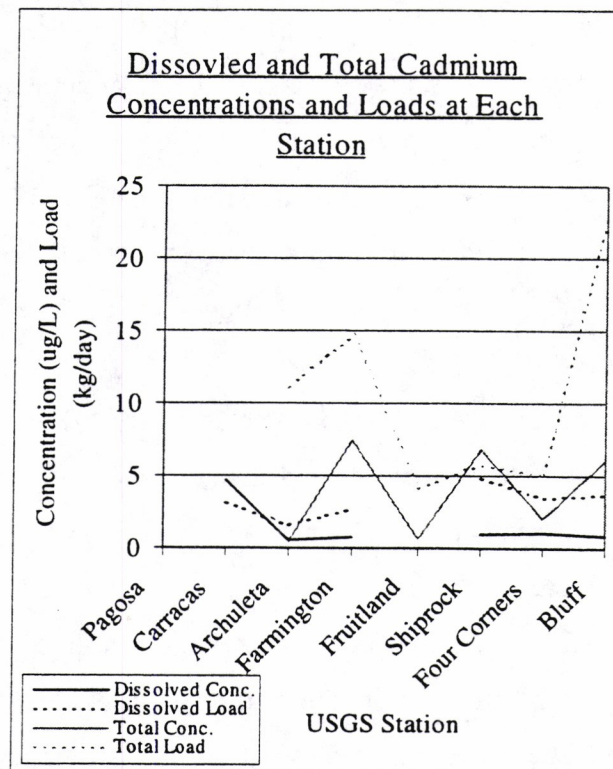


Figure 3: Dissolved and total cadmium concentrations and loads along the San Juan.

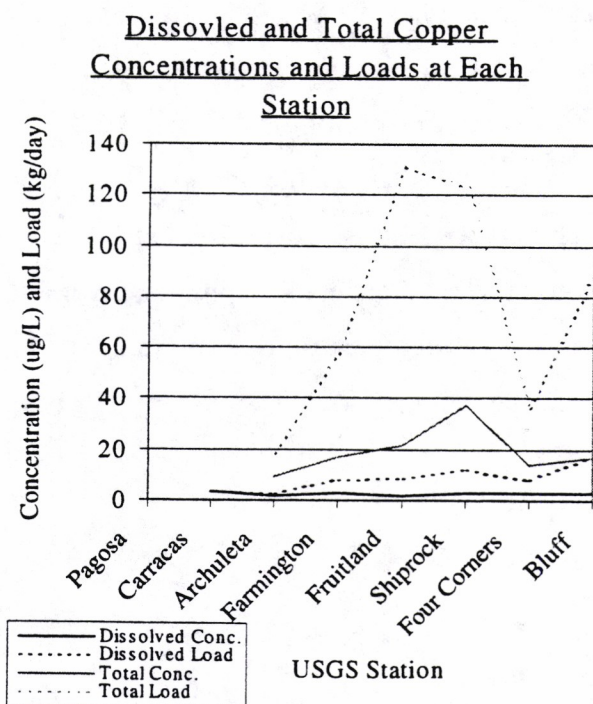


Figure 4: Dissolved and total copper concentrations and loads along the San Juan.

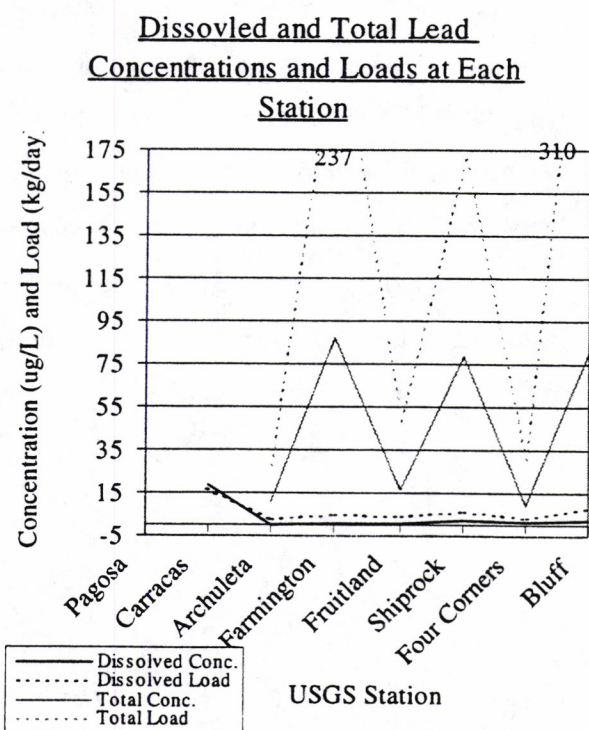


Figure 5: Dissolved and total lead concentrations and loads along the San Juan.

Dissovled and Total Manganese
Concentrations and Loads at Each

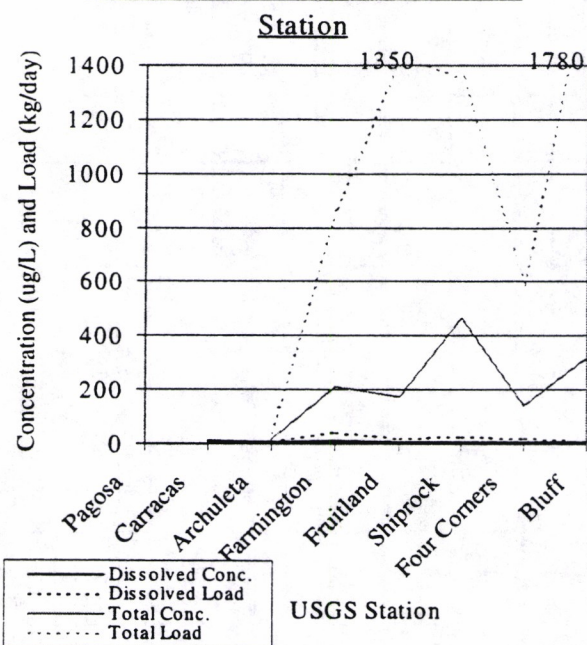


Figure 6: Dissolved and total manganese concentrations and loads along the San Juan.

Dissovled and Total Molybdenum
Concentrations and Loads at Each

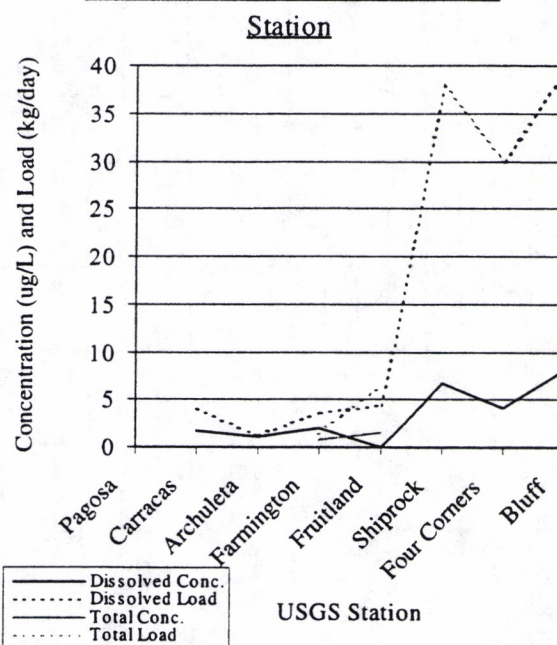


Figure 7: Dissolved and total molybdenum concentrations and loads along the San Juan.

Dissovled and Total Zinc
Concentrations and Loads at Each

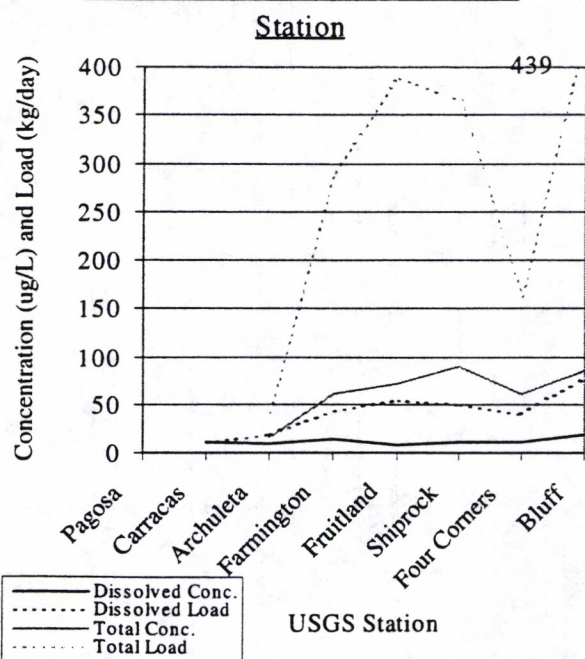


Figure 8: Dissolved and total zinc concentrations and loads along the San Juan.

Water Quality Properties at Each
Station

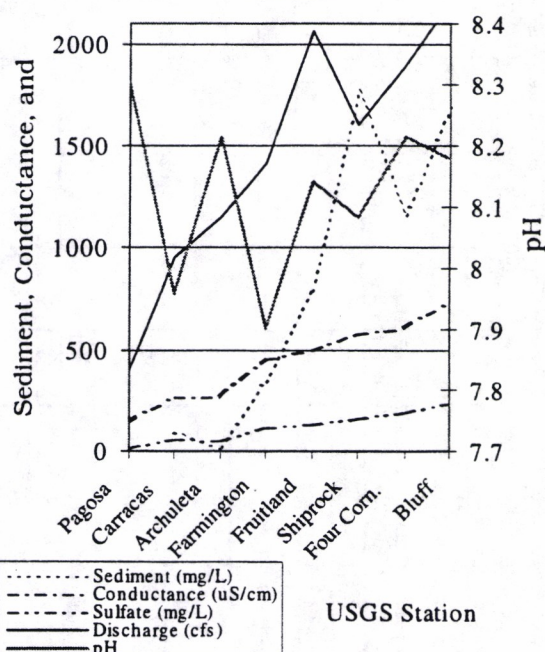


Figure 9: Non-metallic water quality properties along the San Juan.

		East Fork	San Juan @ Pagosa Springs	Navajo @ Edith	San Juan nr Carracas	Piedra @ Arboles	Los Pinos @ La Boca	San Juan nr Archuleta	Canon Largo nr Blanco	Animas @ Farmington	San Juan @ Farmington	La Plata nr Farmington	San Juan nr Fruitland	Chaco nr Waterflow	San Juan @ Shiprock	Mancos nr Towaoc	San Juan @ Four Corners	McElmo nr Bluff	South Creek nr Monticello	Recapture nr Blanding	Cotton Wood nr Blanding	San Juan nr Bluff
Arsenic	Diss. Conc. ug/L			7.0	38.5	39.0	4.5	1.0	2.0	1.0	1.0	1.0	1.1	1.8	1.0	0.9	1.0					1.2
	Diss. Ld. kg/day			0.7	42.2	15.4	2.2	2.4	1.0	1.2	2.8	0.0	5.0	0.1	4.8	0.0	5.9					5.8
	Ttl. Conc. ug/L		1.0			1.5	0.8	1.0	48.8	2.0	1.6	2.0	1.3	16.3	2.6	29.0	2.0					3.0
	Ttl. Ld. Kg/day		0.3			1.1	0.3	2.5	13.0	3.5	6.7	0.1	4.5	0.6	9.2		15.1					9.1
Cadmium	Diss. Conc. ug/L			6.7	4.7	8.1	1.8	0.5	0.7	0.7	0.7	1.0		0.8	1.0	1.0	1.1					0.8
	Diss. Ld. kg/day			0.8	3.1	3.0	0.9	1.6	0.5	1.1	2.7	0.0		0.1	4.9	0.0	3.5					3.8
	Ttl. Conc. ug/L		1.0			1.0	0.8	0.4	1.2	4.9	7.5	1.0	0.6	5.2	6.8		2.0					6.0
	Ttl. Ld. Kg/day		0.3			0.8	0.3	11.1	1.8	7.3	14.7	0.0	4.1	0.3	5.7		5.1					22.9
Copper	Diss. Conc. ug/L			5.3	3.3	4.2	3.7	1.5	4.0	2.7	3.1	3.5	1.9	4.0	3.2	2.0	3.0					3.0
	Diss. Ld. kg/day			0.9	3.4	2.2	2.0	3.0	3.2	4.4	8.2	0.0	8.8	0.4	12.5	0.1	8.2					17.3
	Ttl. Conc. ug/L		23.5			12.0	4.8	9.4	326.6	12.0	17.0	9.0	21.4	38.5	37.3		14.0					17.0
	Ttl. Ld. Kg/day		8.3			10.2	2.2	18.1	684.1	18.0	57.3	0.6	131.5	4.9	123.3		36.0					88.8
Lead	Diss. Conc. ug/L			29.0	18.9	21.4	9.5	0.4	2.2	1.4	0.5	3.0	1.0	1.8	1.9	1.0	1.6					2.1
	Diss. Ld. kg/day			4.2	17.3	9.9	7.2	3.0	1.0	2.3	5.2	0.0	4.3	0.2	6.6	0.0	3.7					7.8
	Ttl. Conc. ug/L		8.0	170.0		5.5	2.9	10.6	134.0	38.0	87.5	8.0	16.3	140.0	78.7		9.5					81.0
	Ttl. Ld. Kg/day		2.3	27.5		4.7	1.1	28.0	310.4	52.3	237.9	0.0	48.4	5.5	170.9		30.5					310.5
Manganese	Diss. Conc. ug/L			14.0	12.3	13.0	17.8	4.3	20.0	26.6	13.5	103.0	6.3	7.0	7.0	85.0	5.7					3.4
	Diss. Ld. kg/day			2.6	10.4	7.9	9.0	11.3	10.2	37.2	42.4	1.2	19.6	0.8	25.6	0.7	21.8					12.4
	Ttl. Conc. ug/L		35.0			30.0	92.5	15.2	14339.3	181.0	210.0	960.0	172.5	325.0	467.8		140.0					320.0
	Ttl. Ld. Kg/day		10.8			24.8	40.6	38.8	35836.2	244.8	867.9	10.6	1439.5	66.1	1351.5		590.9					1776.2
Mercury	Diss. Conc. ug/L				1.7	1.7	1.0	1.0	6.0	7.0	2.0	2.7	0.0	68.0	6.7	3.3	4.1					8.1
	Diss. Ld. kg/day				4.2	4.3	0.4	1.2	2.5	11.7	3.7	0.1	4.4	18.5	37.8	0.1	29.9					39.5
	Ttl. Conc. ug/L						0.8		0.7	0.7	0.7	3.6	1.5	39.4			3.4					
	Ttl. Ld. Kg/day						0.3		0.4	0.3	1.3	0.1	6.6	15.7			13.6					
Zinc	Diss. Conc. ug/L			9.7	10.8	15.0	6.5	9.0	35.0	14.0	14.7	11.9	7.5	12.4	10.5	6.7	10.9					19.2
	Diss. Ld. kg/day			1.6	11.2	6.9	3.3	17.9	20.4	21.4	43.8	0.1	53.8	1.4	49.6	0.3	41.0					78.2
	Ttl. Conc. ug/L		20.0			15.0	7.5	15.0	505.0	99.0	60.0	40.0	71.9	130.0	90.0		60.0					85.0
	Ttl. Ld. Kg/day		6.5			11.3	2.9	40.4	828.3	155.5	290.7	1.9	389.1	20.7	366.3		163.4					439.8
Non-Metallic	Alk mg CaCO ₃							80.7		146.7			110.4	148.5	120.8		125.4					124.0
	Discharge cfs	184.4	400.7	66.0	947.8	519.5	207.0	1148.4	153.5	712.4	1410.4	27.9	2064.9	21.0	1600.0	27.0	1892.2	49.7	0.4	0.1	3.2	2211.1
	Hard. mg CaCO ₃			96.1	107.6	125.0	95.6	100.2	592.5	253.8	162.9	760.9	157.3	606.9	200.2	853.1	209.1				228.5	274.7
	pH		8.3	7.9	8.0	8.1	8.3	8.2	7.9	8.2	7.9	8.1	8.1	8.2	8.1	8.0	8.2				7.8	8.2
	Sediment mg/L			28.0	92.0	48.4	72.0	12.2	22000.0	856.5	335.5	552.8	788.6	3907.5	1760.0		1159.1				25600.0	1680.0
	Sediment kg/day			2.8	126.4	47.3	22.3	22.2	15023.9	3879.0	1440.0	97.2	4255.0	277.0	11505.0		5636.0				535.0	20150.0
	Sp. Cond. uS/cm	114.0	136.7	241.5	262.1	277.7	227.7	266.9	3090.6	601.1	455.3	1833.4	499.6	1513.3	577.6	1577.6	610.8	2612.5	293.5	187.0	529.3	730.8
	Sulfate mg/L		17.0	48.6	57.2	58.2	16.0	48.9	2294.7	153.0	119.1	809.7	131.8	552.5	161.6	738.5	186.7				44.0	236.1

Figure 10: Table of typical dissolved and total metal concentrations and loads and non-metallic properties by station.

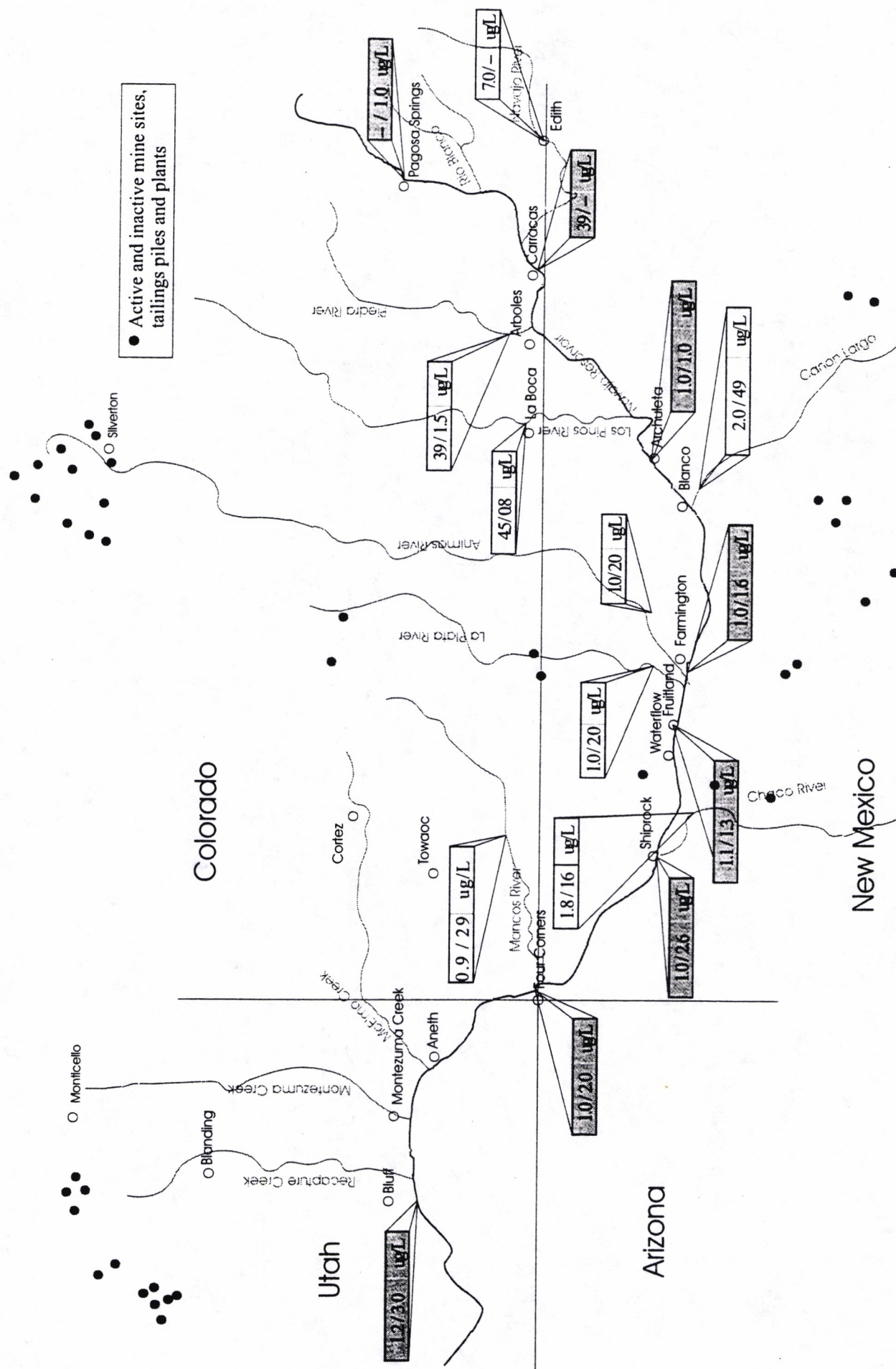


Figure 11: Arsenic concentrations along the San Juan, dissolved / total concentrations at each station along the San Juan and tributaries.

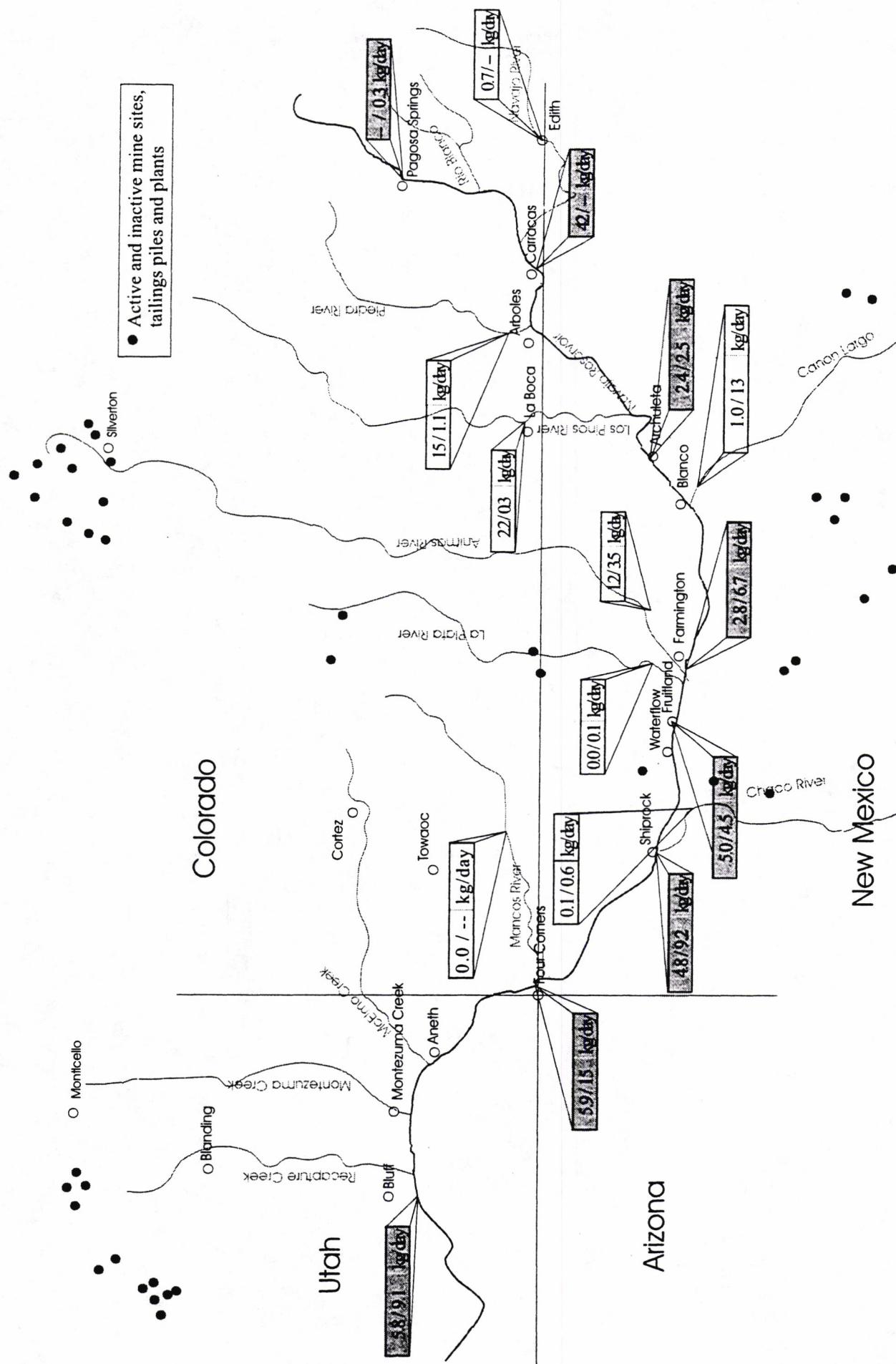


Figure 12: Arsenic Loads Along the San Juan; dissolved / total loads at each station along the San Juan and main tributaries.

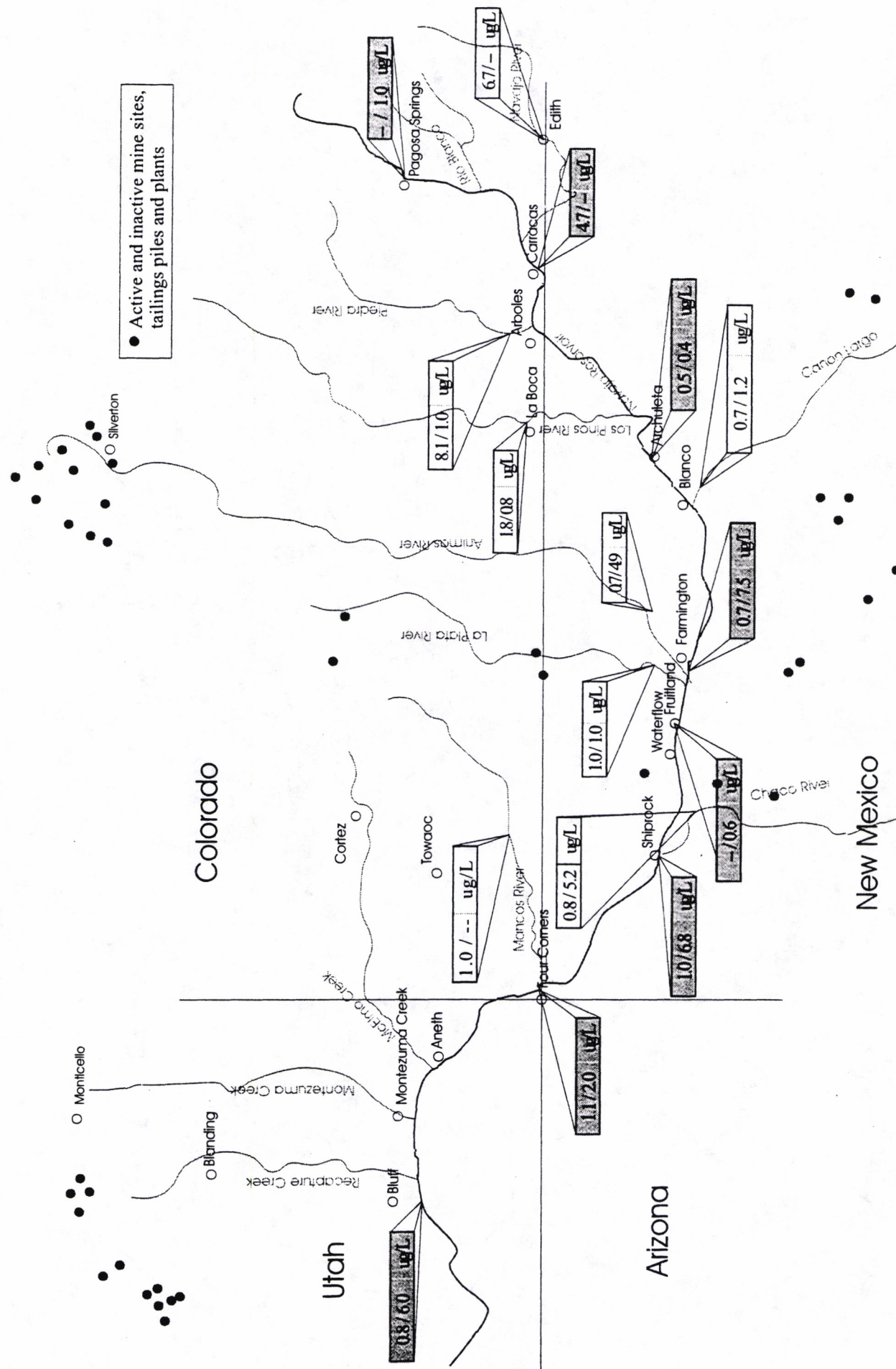


Figure 13: Cadmium concentrations along the San Juan, dissolved / total concentrations at each station along the San Juan and tributaries.

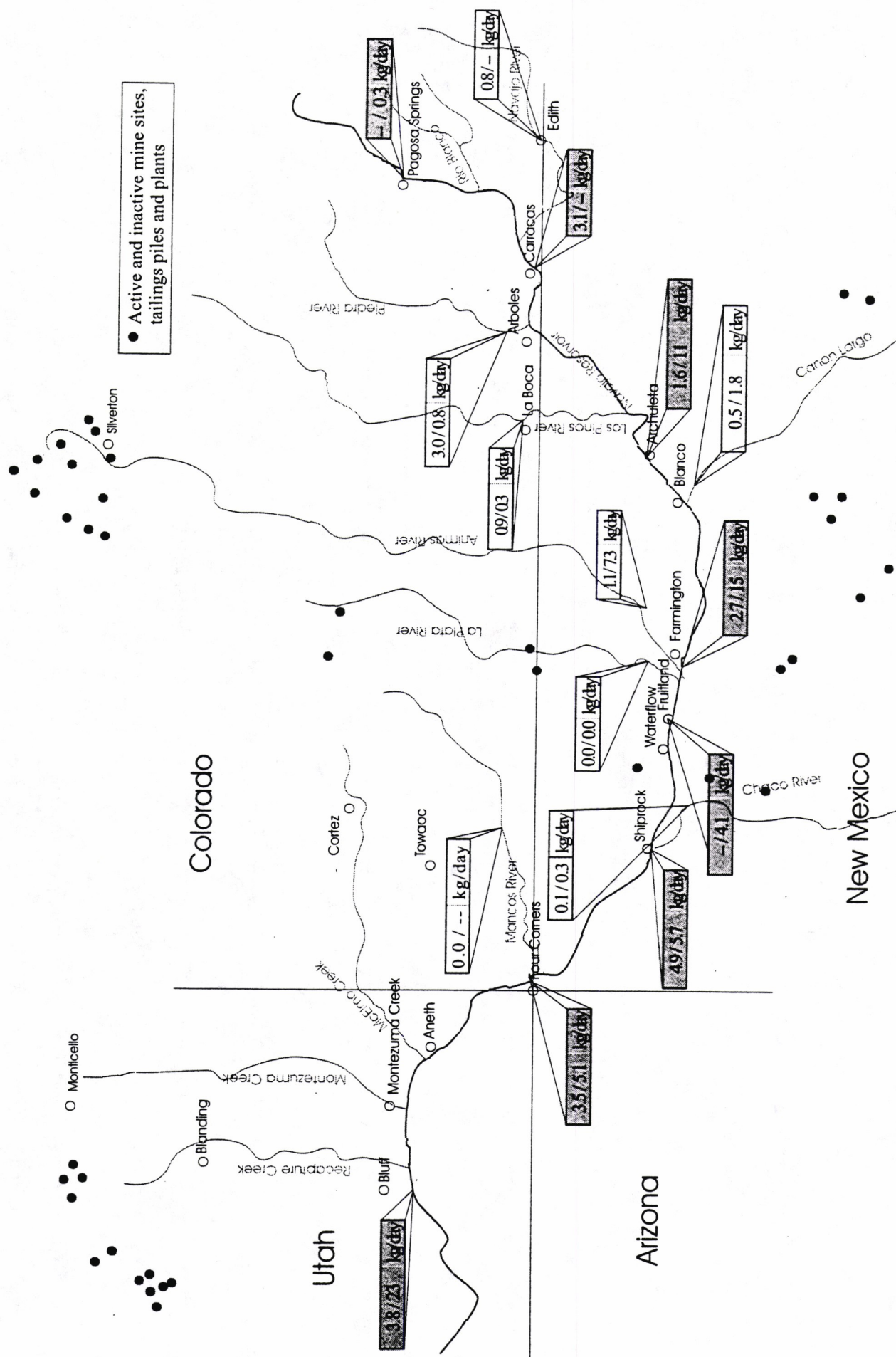


Figure 14: Cadmium loads along the San Juan, dissolved / total loads at each station along the San Juan and tributaries.

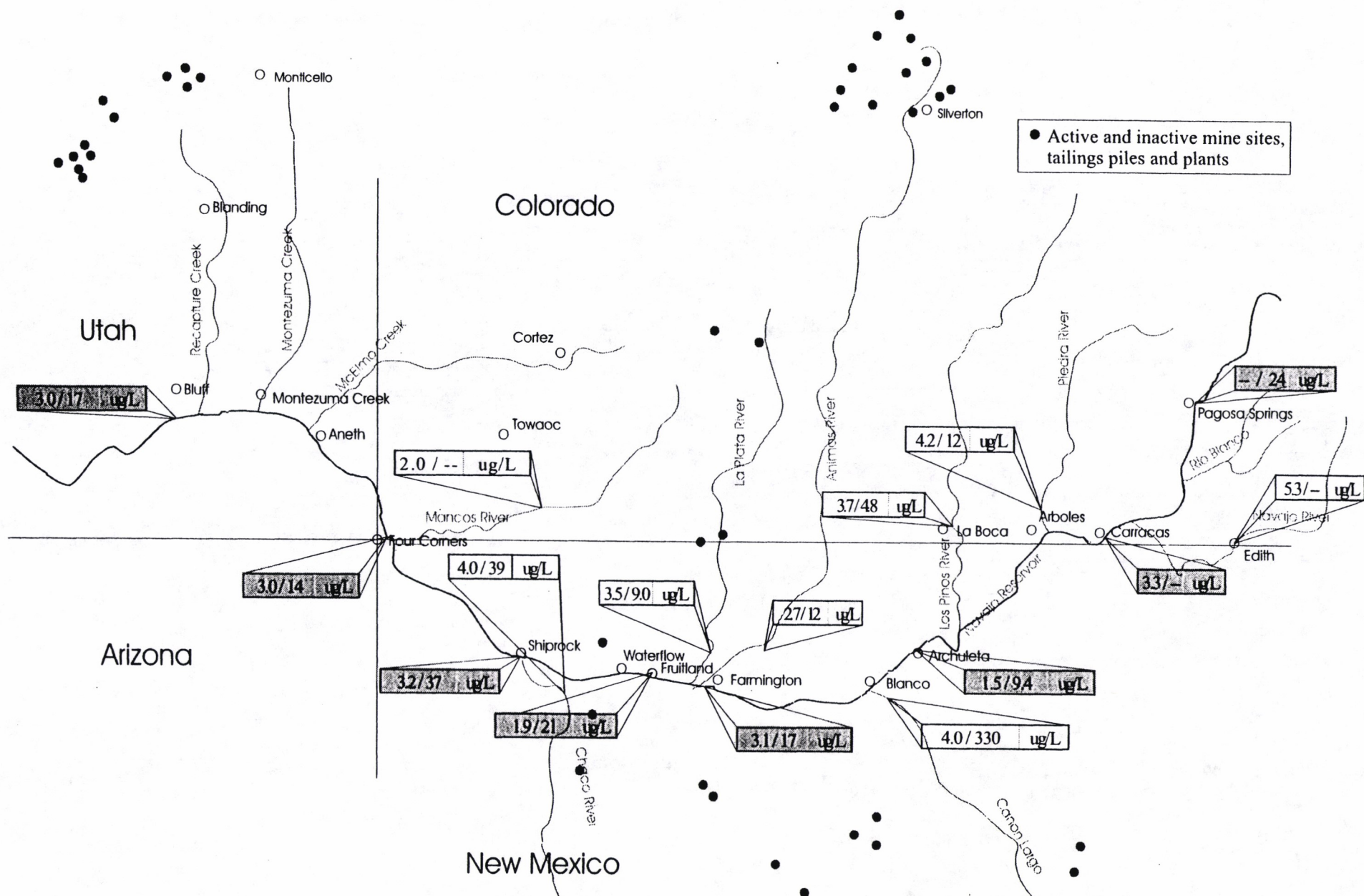


Figure 15: Copper concentrations along the San Juan, dissolved / concentrations at each station along the San Juan and tributaries.

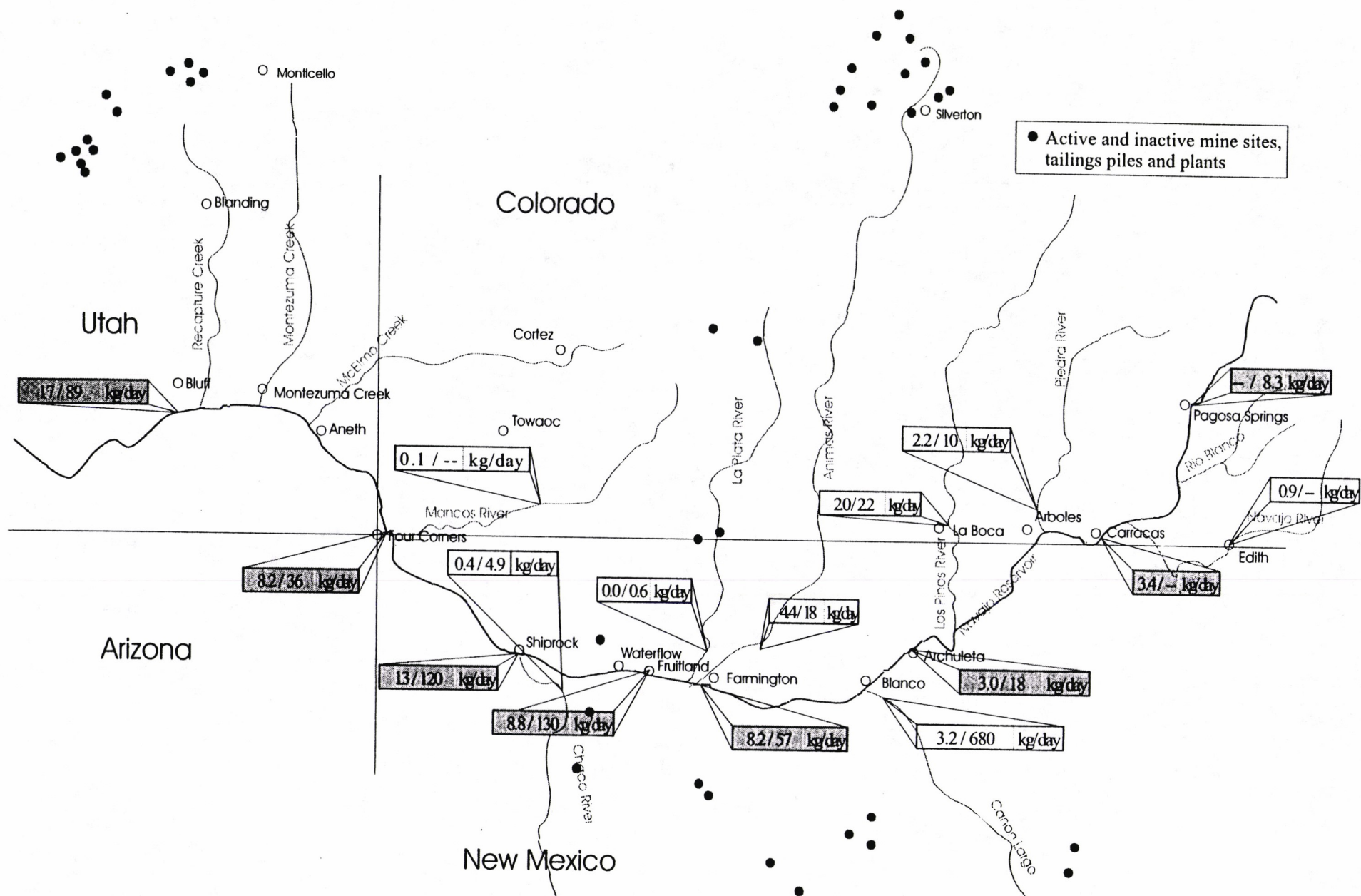


Figure 16: Copper loads along the San Juan, dissolved / total loads at each station along the San Juan and tributaries.

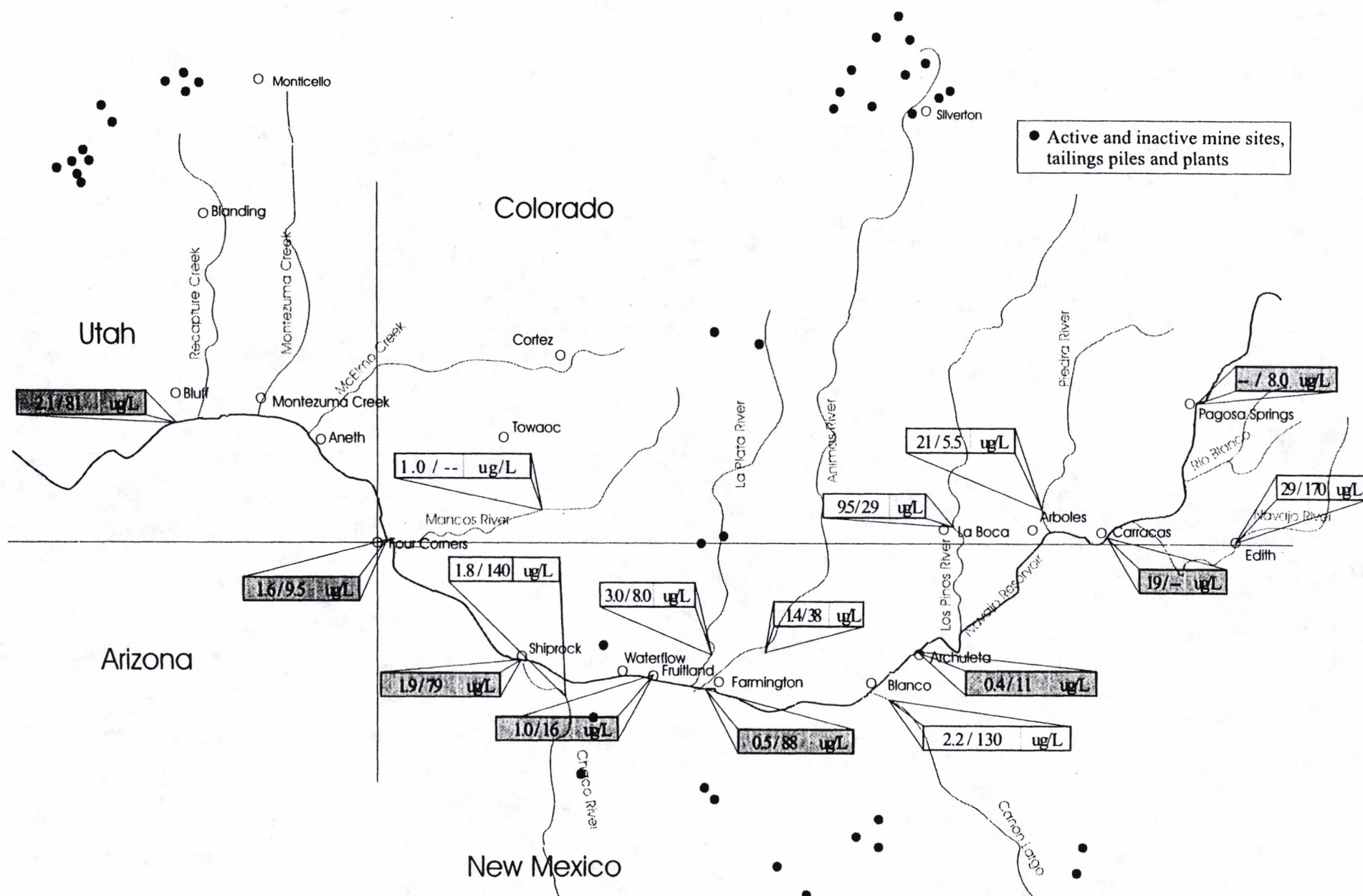


Figure 17: Lead concentrations along the San Juan, dissolved / total concentrations at each station along the San Juan and tributaries.

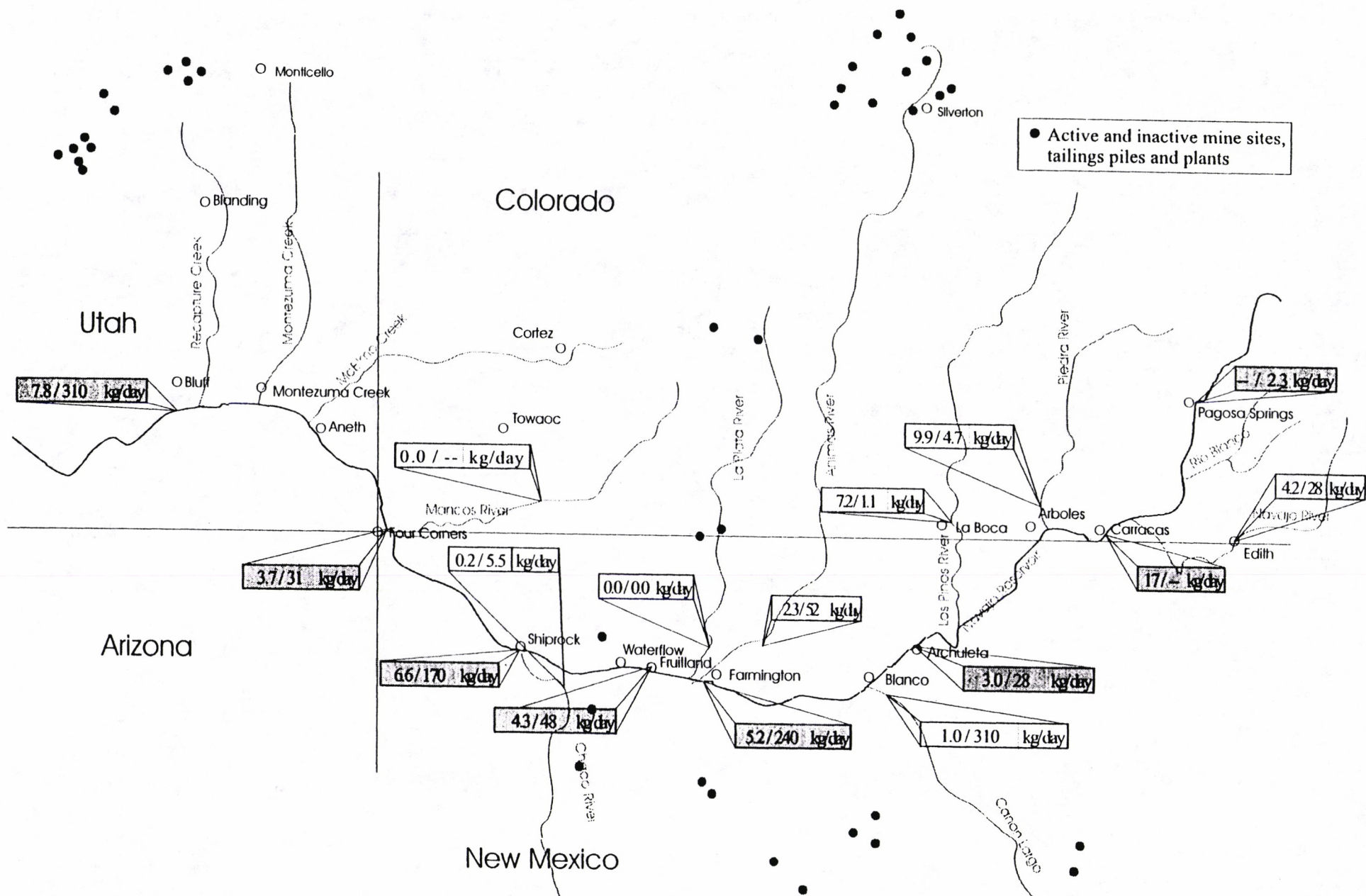


Figure 18: Lead loads along the San Juan, dissolved / total loads at each station along the San Juan and tributaries.

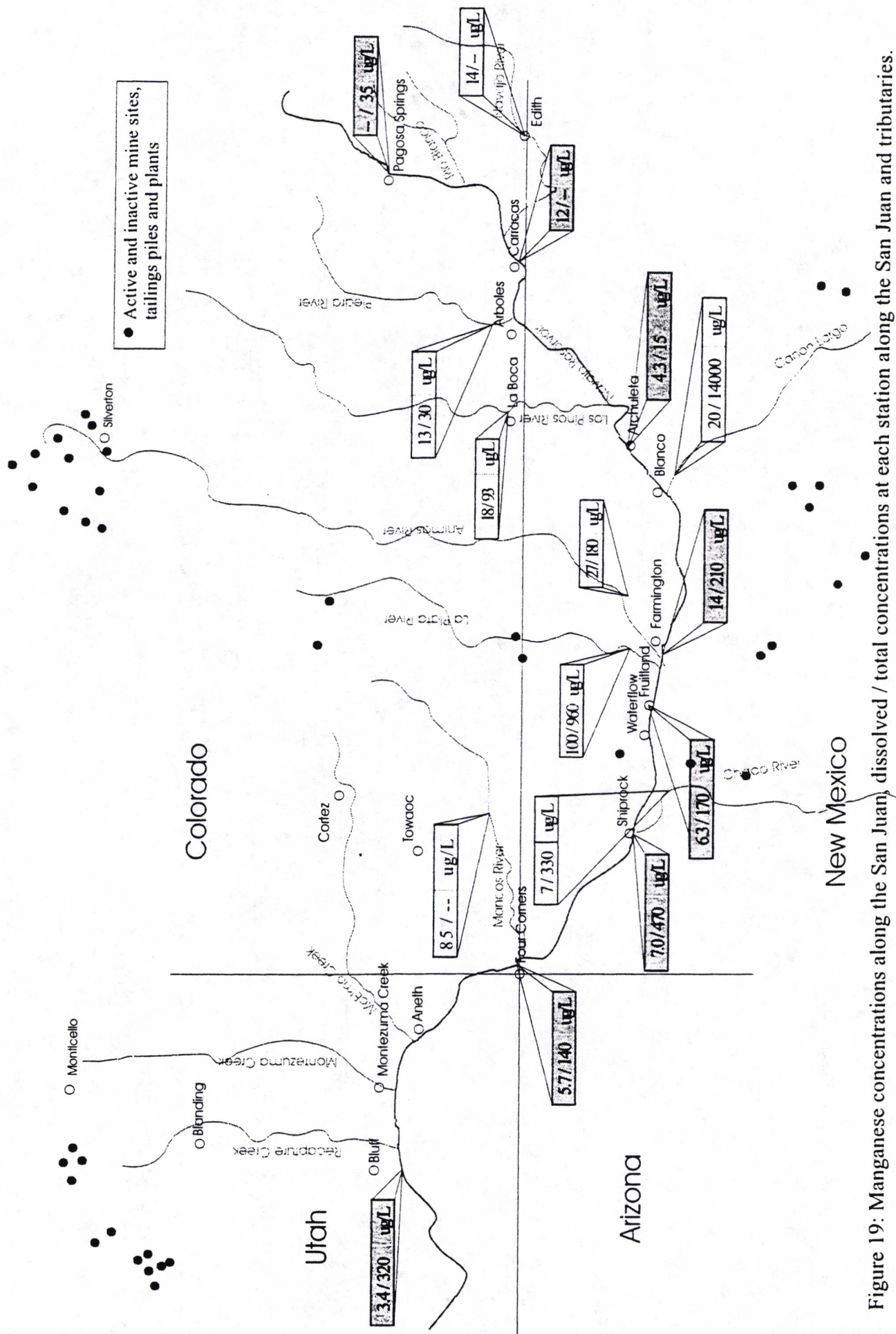


Figure 19: Manganese concentrations along the San Juan, dissolved / total concentrations at each station along the San Juan and tributaries.

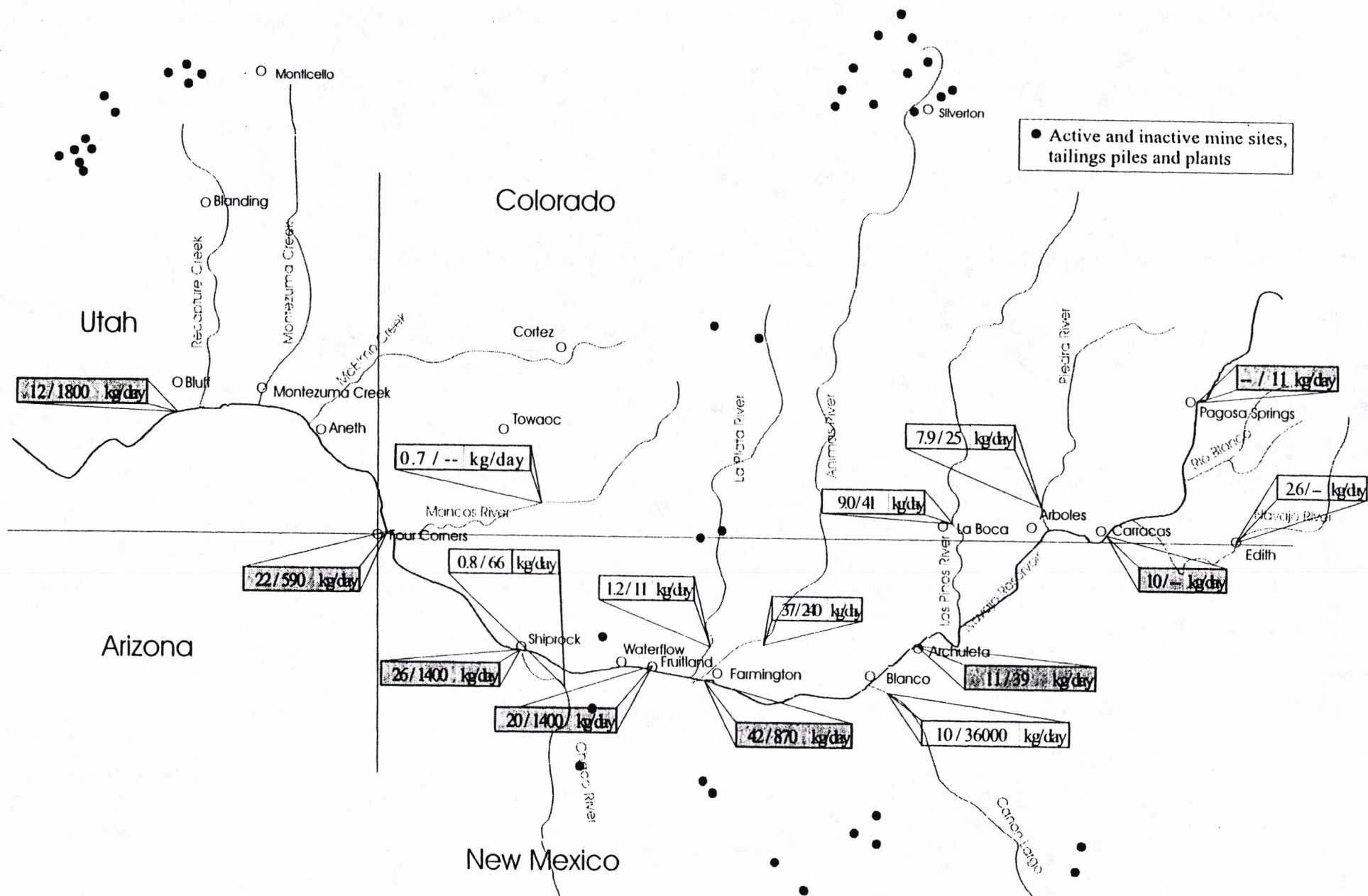


Figure 20: Manganese loads along the San Juan, dissolved / total loads at each station along the San Juan and tributaries.

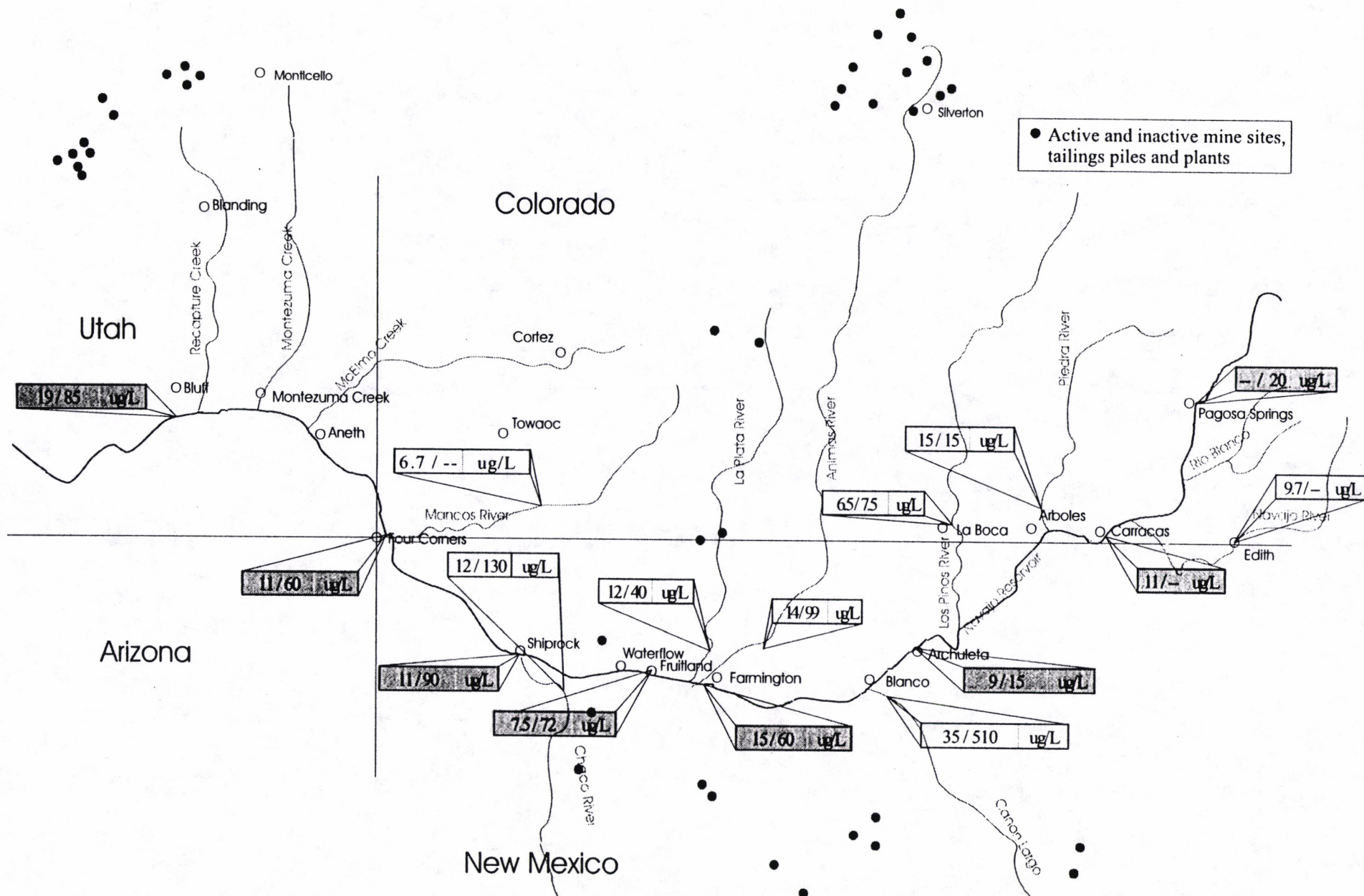


Figure 21: Zinc concentrations along the San Juan, dissolved / total concentrations at each station along the San Juan and tributaries.

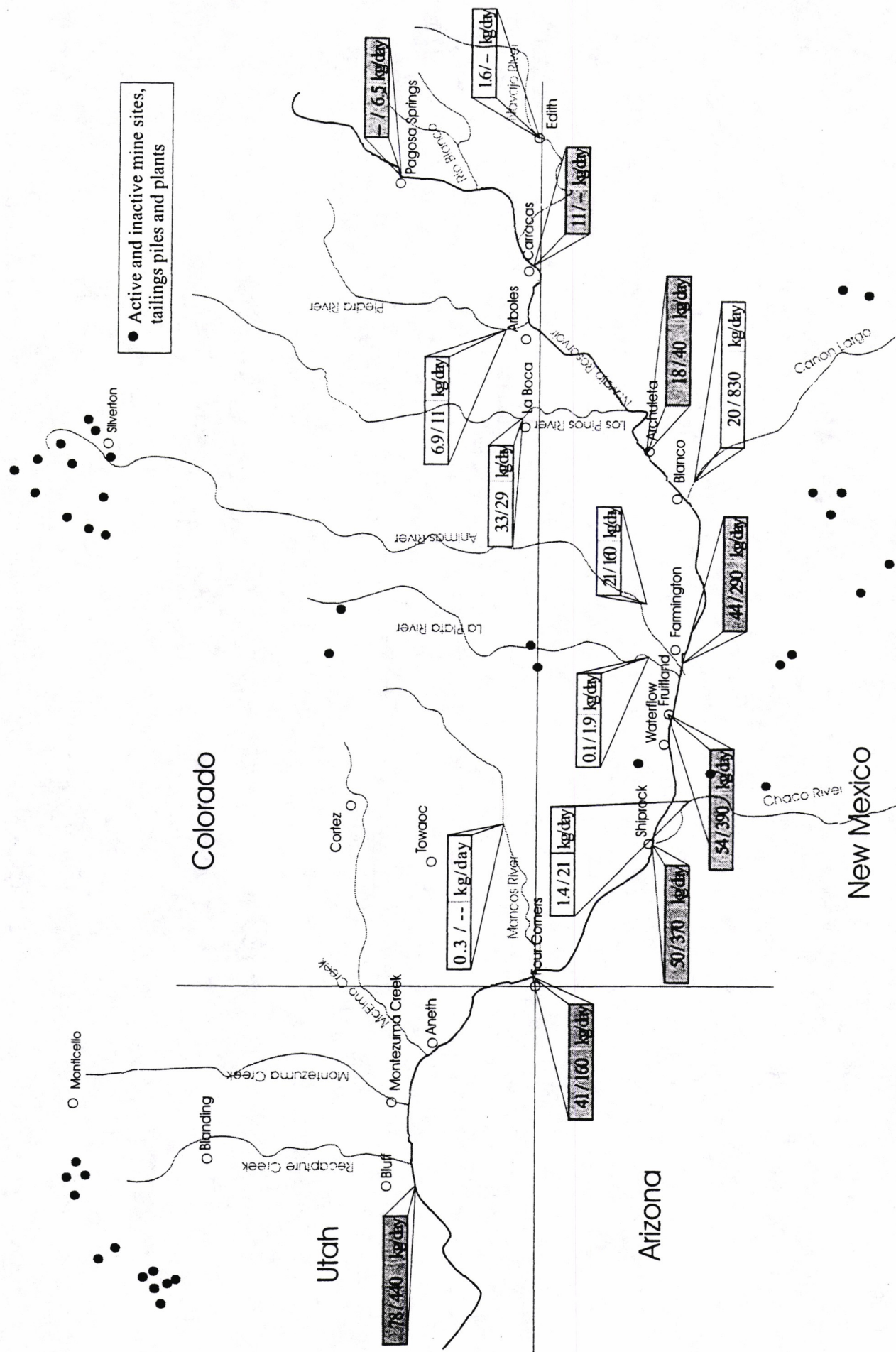


Figure 22: Zinc loads along the San Juan, dissolved / total loads at each station along the San Juan and tributaries.

4.0 DISCUSSION

4.1 INTERPRETATION OF RESULTS

The graphs indicate the total loads and concentrations fluctuate more than the dissolved state. With the exception of arsenic, cadmium, and lead the metals appear to peak at the Fruitland station dropping off abruptly at Four Corners and then increasing again at Bluff. The peak at Fruitland makes sense due to the heavily mined headwaters of the Animas River which joins the San Juan upstream of the station. The drop in metals at Four Corners corresponds with a drop in sediment load suggesting a relationship. The discharge drops by over 400 cfs between Fruitland and Shiprock and then picks up another 300 cfs before Four Corners. One possibility is that metals may have been removed before Shiprock through water diversions and the subsequent inflows had low metal concentrations resulting in a drop in levels. No major mines exist in the area though the specific conductance of the Mancos River read high and the metal concentrations run comparable to the rest of the basin. The river span before Bluff contains several mine inputs which could explain the increase. These hypothesis work only for zinc, manganese, molybdenum, and copper. Arsenic, cadmium, and lead behave differently.

The Arsenic values at Carracas are probably not accurate due to a scarcity of data so the initial large values should be disregarded. Cadmium and lead appear to oscillate with stations reporting alternating high and low values. While the record for cadmium contains some gaps the peaks and lows for lead and cadmium occur at the same stations. The pH varied between 7.9 and 8.3 and the peaks and valleys between stations occur opposite the high and low peaks for cadmium and lead. If a nonspurious relation exists it is unknown. Sulfate, an indicator of possible acid mine drainage, increases steadily over the length of the river but the pH remains fairly high which suggests the mines are not the sulfate source. The specific conductance indicates the river becomes more and more polluted farther downstream. The conductance registers non-metallic as well as metallic properties so will not serve to characterize the river for metals.

The maps of the metal loads and concentrations do not show a cumulative effect from the tributaries as expected. Furthermore the metals do not appear to relate to the location of mines. The upper headwaters of the San Juan have little mining activity yet show significant metal concentrations. Heavily mined areas show similar, lower, or higher concentrations and loads depending on the metal and the location.

4.2 CONFIDENCE IN RESULTS AND SOURCES OF ERROR

The final data table of summaries appears deceptively thorough. While some of the numbers have a sound basis with large amounts of background information, other numbers may have been derived from only one or two points. Before relying on the summary table the individual yearly values for the station in the appendix should be consulted. Further caution is warranted even with this breakdown, since some of the yearly numbers may be from one or two values only. While some conclusions can be drawn, the nature of the data collected undercuts the reliability for anything more than a general idea for further work. Typically the records downstream of Archuleta contain larger, more complete records. Some of the metal values for the Colorado portions of the river are based upon one or two points over the entire 30 year time span.

The first problem with the data analysis was gaps in the data set both in time and in space. The time gaps may continue for several years in a row and vary between the stations. This creates problems since an abnormal year recorded at one station may be neglected at another. The years compared may not fall under the same flow regime or mining activity. The average values taken assumes that the metals at each station did not change significantly in time. Correlation calculations between the date and the constituent values suggest this assumption is warranted in most cases but stations where only one or two points were available do not provide a large enough set for definite conclusions. Each individual year value was examined so the year values in the appendix are statistically sound but the average across the years may not represent current values if the quantities of metals were decreasing or increasing over the years. The collection dates differed from year to year as well as from station to station within a year. The hydrograph for the years would need to be examined in order to determine how the sampling times matched with flows and whether the measurements were consistent between stations and from year to year with respect to the hydrologic cycle. A correlation between discharge and concentration yielded no relation but the seasonal nature was unaccounted for. The frequency of the data also poses another issue. Around 1977 most of the stations shifted from a three times a year sampling two a four times a year pattern during the years when sampling occurred. Some stations still had only one or two records and the sample dates were not uniform along the length of the stream.

Changes in test methods and detection limits create more validity issues. In cases where the tests resulted in a non-detect, 70% of the detection limit was used to be the value of the metals with the idea that this would least affect the statistics. As new and better technology developed, the detection limit lowered. In the case of lead the detection limit before 1977 was 200 micrograms per liter resulting in frequent nondetects which took on a statistical value of 140. Later more sensitive tests show values at that station to run around 10 micrograms per liter. The 140 from early times most likely falsely biases the results but a couple large numbers during the more sensitive testing periods make the 140 value a viable possibility. Non-detects occurred frequently enough to change some of the yearly values significantly but probably do not generally affect a qualitative analysis.

The data failed some internal checks as well. The dissolved constituent sometimes computed to a value greater than the total. One possible cause for this discrepancy might have been the statistical methods. By filling in gaps across the years using means and medians, the dissolved and total values might actually represent different time periods. Unfortunately some cases reported the discrepant values on the same sample date and location. Where this problem occurred the dissolved and total values were treated as separate constituents with no link to each other and the problem became part of the standard error and variability in the tests rather than a logical stumbling block. Several extremely large outlying values occurred. These values may represent storm events, spurts of mine activity, or test error. Rather than discarding odd data, the points were compensated for by taking the mean or median value depending on the skewness of the data.

The important consideration to remember when reading this data is that the final values came from the assumption that whatever data was present would generate accurate typical values. Sparse data sets for some locations make that assumption shaky. The system is either too complex for this level of analysis or the final results are misleading. These results should be taken and used with a grain of salt for qualitative analysis rather than quantitative.

Of the techniques used to attempt to make sense out of the statistical results the basic story is unsuccessful. Ratios and correlations did not yield any conclusive patterns and the indexing attempts typically failed to hold even throughout the different years at a single station. Very little indexing experience or familiarity was present so an indexing technique may yet prove fruitful.

4.3 FUTURE RECOMMENDATIONS

The techniques used in this project were unable to generate concrete reliable data. A different approach to the problem might achieve better results. The first recommendation would be to examine a smaller area. The time frame for this study precludes detailed analysis of the land use and characteristics along the length of the river. The data shows that the interaction along the stream contains a high degree of complexity which does not behave entirely intuitively from the data available. A smaller area would allow more in depth examination and understanding of the surrounding and in stream conditions. Secondly, a more complete historical record would be recommended. Possible sources for this information might be consulting firms or state agencies other than the USGS. The method for analysis should also change. This reported attempted to evaluate the information with a purely statistical approach. Other watersheds or case studies should be researched and their techniques used and adapted as necessary. Though indexing proved futile in this study the authors lack of experience does not preclude a future successful technique. A successful indexing method may help to gloss over gaps in data sets and reduce the complexity of the analysis.

5.0 CONCLUSION

The results from this analysis make large assumptions about the typical value for metal concentrations and loads in the river. The sparse data makes for unreliable final figures. Unfortunately inconsistencies in the historical records used in the analysis such as time discontinuities and changes in the tests throw doubt on the usefulness of quantitative data. Several qualitative conclusion still can be drawn. No concrete relation between the tributary inflows and the main river metals was apparent. The location of the mining activity and the concentrations and loads appear to have a passive relation if any at all. In general the system appears too complex to characterize an entire river. Future attempts should look at smaller sections where the ecology, geology, and human activities can more completely be classified and related.

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SUMMARY

Mining related water quality studies most commonly report results for stations immediately below the mining activity. Water quality data from stations located further downstream are usually not part of the original mining-related study.

Most studies are done by the U.S. Geological Survey and emphasize sampling and analysis. Water quality sampling most often occurs near major population centers, on federal lands in the western United States where historic mining has occurred, and usually during the summer months when field sites, particularly higher elevation sites, are more accessible.

Two studies looked at heavy metal concentrations and streamflow. Metal fluxes were not additive and could not be used to assess downstream changes (Folsom, 1998). Heavy metal concentrations usually have a flow dilution function with streamflow, as streamflow increases metal concentrations decrease. Some inter-annual variation in heavy metal concentrations appeared to be a function of different hydrologic conditions or streamflows, rather than mining activities (Mooney, 1997).

The U.S. Geological Survey is the lead federal agency for water quality monitoring, but other federal or state agencies participate in water quality monitoring as well. Water quality data from different sources are often not directly comparable, and cannot be easily merged into one data base. Inconsistencies or differences included:

- stream discharge not always measured, thus metal loads or fluxes could not be calculated.
- water quality hardness or alkalinity not always measured, preventing calculation of metal species and hence toxicity or compliance with water quality standards or criteria.

- change in metals analyzed, metals analyzed changed between stations.
- change in filter size for dissolved metal analysis, the operational definition is .45 microns, but reported pore diameters ranged from 0.45 microns to 10,000 atomic mass units.
- water quality sample preparation for total metal analysis ranged from rigorous acid digestion with heat to acid addition only.
- water quality analyses that are below detection were not uniformly recorded, detection limits change with the individual labs and with changes in analytical technology, but some agencies report these values as zero, while others report the values as one-half or even as the detection limit (U.S. Environmental Protection Agency, 1998).

Factors that contribute most to the development of acid mine drainage are mineral deposit type, geologic setting, and size of the disturbance. Acid mine drainage is more apt to develop from a mineral deposit with large quantities of fine-grained pyrite, large volumes of disturbed minerals-overburden and tailings, and occurs in rocks that have a low acid neutralizing capacity (U.S. Geological Survey, 1998). Water quality studies usually do not report mineral deposit or deposit quality since these data are often proprietary information for the developer.

Mining influences on water quality may be more of a function of the ore source and its proximity to surface water than other factors. Water quality changes observed from mining activities suggested that the larger operations near surface water were more apt to influence water quality than smaller operations away from water sources. Water quality influences appear minimal if best management practices are employed. Water quality studies did not identify if best management practices were used in the mining operation. It is difficult to develop a unifying principle of water quality effects from an abandoned mine site with water quality effects from an

active mine using best management practices. An abandoned historic mine site with uncontrolled acid mine drainage cannot be used to evaluate a current cyanide heap leach operation.

The U.S. Geological Survey reported that the 65,900 metal mining entries located west of the 102° longitude approximately 25,000 had historic mining production. The majority of the entries were exploration workings, not production mines. Water quality monitoring efforts could not separate exploration impacts from production-related impacts (USGS, 1998). The USGS research effort had significantly more resources than this Forest Service funded effort, but we both came to the same conclusion that initial geospatial analysis of available data indicate that measures of water quality are insufficient to characterize water quality at the watershed scale.

At the watershed scale, existing water quality databases do not accurately portray the influence of mining and related activities on surface water quality (USGS, 1998). It is doubtful that a universal model can be developed to identify the potential effects of mining and related activities on water quality. Heavy metal concentrations in stream sediments may be a better indicator of mining water quality impacts (Hazel, 1998). It appears that water quality data should be used with other environmental monitoring efforts, and land uses to best predict if mining and its related activities affect water quality.

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Objective 3. Summarize available data on an 8 digit watershed basis.

As shown earlier, water quality data are insufficient to portray the influence of mining activities on a watershed level. Site-specific studies in the Upper Arkansas river and the San Juan River basins failed to identify spatial or temporal characterization (Folsom, 1998 and Mooney, 1997). Our conclusion was that water quality characterization of the influence of mining and related activities cannot be done on an 8 digit watershed level with the existing water quality data bases. This is based on our inability to characterize water quality in 11 or 14 digit watersheds as influenced by mining-related activities; a finding similar to other recent studies (USEPA, 1998 and USGS, 1998).

Several factors compound the characterization of water quality as affected by mining-activities. These include: sampling location and frequency, water quality parameters, mining location, identification of best management practices, and length of water quality records. A brief description of each follows.

As discussed under Objective 2, most water quality sampling for assessment of the influence of mining on water quality is conducted by the federal government. Sampling locations have tended to be near populated areas, and surprisingly few water quality samples are collected during the winter season. Most sampling locations tend to be immediately below the mining-related activities, and few studies have been designed or conducted to access off-site effects on water quality.

Off-site sampling or sampling locations farther downstream from the mining-related activity are usually not related specifically to the mining activity. Water quality parameters

measured tend to reflect the original purpose of the water quality effort at a station and not as a network. This is particularly true for heavy metals, both dissolved and total fractions. Time between sampling events ranged from 1 week to 1 year, depending on the river basin sampled. Variability in sampling intervals has been acknowledged as contributing to the lack of adequate watershed characterization of water quality as influenced by mining-related activities (USGS, 1998).

From the literature review, we determined that metal concentrations were the best indicators of mining-related activity influences on water quality. Exceptions occur all the time, but metals from a conceptual basis made for the logical choice. Metal concentrations vary with stream discharge. This is often a complex relation. As stream discharge increases, dissolved metal concentrations tend to decrease - a flow-dilution. However, as discharge increases, stream sediments, both colloidal and inorganic, may be transported. The total metal fraction is usually associated with stream sediments, thus total metal concentrations may increase with stream discharge - flow driven (Stednick, 1991). Stream hydrology - both hydrograph shape and flow rates may affect metal concentrations. It is difficult to separate hydrologic influences from mining influences (Stednick and Kern, 1993; Mooney, 1997).

Location of mining related activities in a watershed, like any other land-use, will determine potential water quality effects. If a mine is located near a stream or water course, its potential to affect water quality is higher than if the mine activity was on the watershed divide. From the literature, it was often difficult if not impossible to ascertain the 'hydrologic connection' of the mine to surface waters. In our view, this is essential information needed to characterize water quality.

Ostensibly, any mining activities after 1972 would employ best management practices (BMPs) (see Objective 1). This does not intend to mean that mining activities prior to 1972, did not use BMPs. However, few studies reported on the use (or efficiency) of BMPs. It is unfair to compare water quality as influenced by mining activities with and without BMPs. In our estimation, the literature will never address BMP use, since this may invite culpable negligence or acknowledged violations of the Clean Water Act.

Finally, most studies on the effects of mining related activities on water quality have specific study objectives that are usually short-term. Mining activities may represent a cumulative watershed effect. Characterization of such effects requires a long-term data record. When attempting to compile data over a period of time from different agencies or programs, water quality sampling and analysis issues are usually greater than the data validity (Stednick and Kern, 1993).

In conclusion, water quality portrayal or characterization on a watershed level as influenced by mining related activities could not be done on an 8 digit watershed basis. New spatial analysis techniques coupled with other environmental metrics such as stream sediment (Hazel, 1998), may need to be considered (USGS, 1998).

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